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ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

VOLUME III

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ALLEN'S COMMERCIAL
ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ANALYSIS, AND PROXIMATE
ANALYTICAL EXAMINATION OF THE VARIOUS
ORGANIC CHEMICALS AND PRODUCTS
EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR
THE DETECTION AND ESTIMATION OF THEIR IMPURITIES,
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

VOLUME III

Hydrocarbons, Bitumens, Napthalene and Its Derivatives, Anthracene
and Its Associates, Phenols, Aromatic Acids, Gallic Acid, and Its
Allies, Phthalic Acid and the Phthaleins, Modern Explosives.

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FIFTH EDITION. REVISED AND IN PART REWRITTEN

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PRINTED IN U. S. A.
BY THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

This volume has been fully revised and in part re-written. While there is but little change in its scope, there has been a considerable change in the contributors, all of whom will be recognized as men thoroughly familiar with their subjects.

In the sections of this book bearing on the testing and analysis of tars, pitches and oils, the methods of the U. S. Bureau of Mines and the American Society for Testing Materials have been generally followed.

The article on "Bitumens" was so nearly completed before Dr. S. P. Sadtler's death that but a few minor details had to be supplied by the Editors. The part on "Benzol and Its Homologues," which was formerly included in this section has been transferred. It has grown so considerably since the World War, that it was decided to treat it separately along with "Dye Intermediates and Dyes," in what, doubtless, will be Volume VI. If this step had not been taken the present volume would have been a rather large one.

The sections on "Napthalene" and "Anthracene" contain the latest methods of testing the crude and refined products that are in use commercially at the present time.

The contribution on the subject of "Phenols" represents considerable new work, and there will be found in this section practical analytical methods for separating isomeric cresols and cresols from phenol. The Rydeal-Walker and Hygienic Laboratory Methods for determining the phenol co-efficient of antiseptics are given in full.

In the article on "Phthalic Acids," modern work on the subject of indicators is discussed, and the use of indicators for volumetric titrations is given and the newer indicators for Hydrogen Ion control work are considered.

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HYDROCARBONS

BY H. E. COX, M. Sc., Ph. D., F. I. C.

Hydrocarbons (*i. e.*, those compounds which contain only carbon and hydrogen) occur in nature ready formed in natural gas, petroleum oil, earth-wax, shale and coal, or are obtained from these and a great number of vegetable substances by ordinary or destructive distillation. Recently, hydrocarbon oils have been found to be natural to certain fish liver oils (See Chapman, *Trans. Chem. Soc.*, 1918, **113**, 408; Tsujimoto, *J. Ind. Eng. Chem.*, 1917, **9**, 1098, 1920, **12**, 73); a point of much importance in the examination of such oils (see Vol. II, p. 298). The fact that these natural products as well as the distillates obtained from them consist invariably of mixtures, mostly of a highly complex character, renders the identification and estimation of the individual compounds exceedingly difficult and in many cases practically impossible.

There are two great classes of hydrocarbons: the Aliphatic or Acyclic hydrocarbons (the paraffins, olefines, acetylenes, etc.) in which the carbon atoms are linked together in open chains, and the Aromatic or Cyclic hydrocarbons (the benzene series, polymethylenes, naphthalene, anthracene, etc.) in which some or all of the carbon atoms form a closed chain or ring. The cyclic hydrocarbons differ materially from the acyclic series; they contain a larger percentage of carbon in the molecule and are remarkable for the stability of their nucleus or the closed chain of carbon atoms. In general, they may be differentiated from the aliphatic hydrocarbons by their action with nitric acid or sulphuric acid which form nitro-derivatives and sulphonic acids respectively, whereas the aliphatic hydrocarbons do not so react, although certain of the paraffins do form nitroparaffins in small quantity with dilute nitric acid. This test may readily be applied by adding 5 c.c. of fuming sulphuric acid to 1 c.c. of the liquid, then gently warming, and after a few minutes pouring the mixture into cold water; if all goes into solution aromatic hydrocarbons are indicated, whilst the aliphatic members, being unaffected, are insoluble. Friedel and Crafts' reaction is also useful for the identification of the two classes: 1 grm. of anhydrous aluminium chloride and 1 c.c. of dry chloroform are added to the same volume of the liquid; on gently warming hydrochloric acid is evolved by aromatic hydrocarbons only.

Although both types of hydrocarbons often occur together in commercial products it is convenient to deal with them separately.

THE ALIPHATIC HYDROCARBONS

These are divided into classes according to the ratio between the number of carbon and hydrogen atoms in the molecule; the most important groups are the paraffins, olefines, di-olefines and the acetylenes.

Fractional distillation offers a means of separating groups possessing similar physical characteristics within certain narrow limits. But even where hydrocarbons of one series, such as paraffin or benzene derivatives are concerned, their quantitative isolation is a very lengthy and tedious operation involving many fractionations on account of the close proximity of the boiling points and the consequent overlapping of fractions. The problem becomes, however, still more complex when hydrocarbons of different series are present and inseparable mixtures of constant boiling point are formed. Thus, the addition of aliphatic to aromatic hydrocarbons exerts a depressing influence, and a small addition of *n*-hexane may lower the boiling point of benzene to 65°. (Jackson and Young, *Trans.*, 1898, **73**, 922.)

A further difficulty is introduced by the instability of the higher members at the temperature at which they boil; distillation is then accompanied by decomposition or molecular changes ("cracking") and must be carried out at reduced pressure or with the aid of superheated steam.

Notwithstanding these limitations, distillation is an indispensable method in examining hydrocarbon mixtures, both for the determination of the boiling range without fractionation of the distillates and for the separation of fractions boiling within more or less narrow limits. The latter operation, by which such complex mixtures as crude petroleum oil or coal tar are resolved into groups of comparative simplicity, almost invariably precedes the application of specific chemical reagents.[1]

The range and number of fractions to be taken depends on the scope of the examination and may vary between wide limits. The specific gravity of each fraction is determined, and often the refractive index, optical rotation, viscosity, flash point, etc., will give useful information. The method may also be applied at low temperatures to those hydrocarbons which are gaseous at ordinary temperatures and pressure.

The application of chemical methods often presents similar difficulties in the treatment of hydrocarbon mixtures. Most specific reagents do not enable the analyst to identify or isolate individual compounds but act only as group reagents. There is also, as in the case of the physical examination, always a tendency for different groups to overlap. For instance, concentrated sulphuric acid, which is frequently used to remove unsaturated compounds from saturated hydrocarbons, is—contrary to statements in most textbooks—capable of attacking paraffin hydrocarbons on prolonged contact and particularly when it contains some sulphuric anhydride; a nitrating mixture, the typical reagent for aromatic hydrocarbons, will also attack naphthenes, and dilute nitric acid converts normal hexane, heptane, and octane into nitro-paraffin on warming (Francis and Young, *Trans. Chem. Soc.*, 1898, **73**, 928; Worstall, *Amer. Chem. J.*, 1898, **20**, 202; Konowaloff, *Ber.*, 1906, ii, 312); similar examples can be found with nearly all the usual reagents.

It is important to remember that nearly all commercial hydrocarbon products, unless highly refined, contain members of different series; thus petroleum oils from practically any source contain, besides aliphatic or naphthene (polymethylene) hydrocarbons, benzene homologues sometimes up to 40% (Jones and Wootton, *J. Chem. Soc.*, 1907, **91**, 1146; J. Stewart, *J. Soc. Chem. Ind.*, 1900, **19**, 986); on the other hand, coal-tar, especially in its lower fractions, comprises a number of aliphatic hydrocarbons. Shale oil distillates are mixtures of chain and cyclic compounds, and spirit from "cracked" oils comprises a variety of hydrocarbons of varying degrees of saturation.

---

[1] For a closer study of the subject see Young, *Distillation Principles and Processes*, London, 1922.

Although the fact of hydrocarbons of different types frequently appearing together seems to justify a *prima facie* case for a systematised series of tests, no such scheme of general applicability has ever been devised. The kind of reagents employed and the sequence of operations must vary according to circumstances. Generally, it will be found useful to proceed in this order: unsaturated aliphatic compounds (olefines and acetylenes) and partially saturated hydroaromatic compounds, aromatic compounds, naphthenes, paraffins. In most cases commercial requirements will not entail a complete examination of a hydrocarbon mixture, but only definite tests for certain properties or components will be specified.

THE PARAFFINS

The Paraffins.—This, the largest of all the groups, includes those hydrocarbons in which the carbon atoms are united only by single linkages (hence called saturated hydrocarbons), and which consequently contain the largest possible amount of hydrogen, the general formula being C_nH_{2n+2}. Its members are formed when carbonaceous matter decays or is decomposed by heat in the absence of oxygen at relatively low temperatures and consequently are found in the emanations from marshes, the gases escaping from ponds, the "blowers" of the coal pits, and in coal-gas, coal-tar, shale oil, etc., as well as in the natural gas of the petroleum districts and in petroleum —particularly that of Pennsylvania; while the higher members ($C_{38}H_{78}$, for example) occur as the minerals ozokerite, hatchettite, ceresine, etc.

Although the first three members of the series each exist in one form only, there are two butanes, three pentanes, and five hexanes, all of which are known, whilst the number of isomerides of the higher homologues theoretically possible is enormous, and for such a substance as $C_{13}H_{28}$ no less than 802 formulæ can be devised. Of the higher paraffins comparatively little is known, few having been obtained in a state of purity, and it is probable that in most cases even the m. p. and b. p. have not been ascertained with any degree of accuracy.

The following table gives some of the physical constants of the normal paraffins, and is taken (with some additions) from Richter's "Organische Chemie" (1919 edition).

	Formula	M. p.	B. p. at 760 mm.	B. p. at 15 mm.	Sp. gr.	
Methane	CH_4	−184°	−164°			
Ethane	C_2H_6	−172°	− 84°		0.446	
Propane	C_3H_8		− 45°		0.536	at 0° C.
Butane	C_4H_{10}		1°		0.600	
Pentane	C_5H_{12}		38°		0.640	
Hexane	C_6H_{14}		71°		0.701	
Heptane	C_7H_{16}		98.4°		0.719	
Octane	C_8H_{18}		125.5°		0.733	
Nonane	C_9H_{20}	− 51°	149.5°		0.746	
Decane	$C_{10}H_{22}$	− 32°	173°		0.775	at their m. p.
Undecane	$C_{11}H_{24}$	− 26.5°	194.5°		0.775	
Dodecane	$C_{12}H_{26}$	− 12°	214°		0.775	
Tridecane	$C_{13}H_{28}$	− 6.2°	234°		0.775	
Tetradecane	$C_{14}H_{30}$	+ 5.5°	252.5°		0.775	
Pentadecane	$C_{15}H_{32}$	+ 10°	270.5°		0.775	
Hexadecane	$C_{16}H_{34}$	+ 18°	287.5°		0.775	
Heptadecane	$C_{17}H_{36}$	+ 22.5°	303°	170°	0.776	
Octadecane	$C_{18}H_{38}$	+ 28°	317°	181°	0.777	
Nonadecane	$C_{19}H_{40}$	+ 32°	330°	193°	0.777	
Eicosane	$C_{20}H_{42}$	+ 36.7°		205°	0.778	
Heneicosane	$C_{21}H_{44}$	+ 40.4°		215°	0.778	
Docosane	$C_{22}H_{46}$	+ 44.4°		224°	0.778	
Tricosane	$C_{23}H_{48}$	+ 47.7°		234°	0.778	
Tetracosane	$C_{24}H_{50}$	+ 51.1°		243°	0.779	
Heptacosane	$C_{27}H_{56}$	+ 59.5°		270°	0.780	
Hentriacontane	$C_{31}H_{64}$	+ 68.1°		302°	0.780	
Dotriacontane	$C_{32}H_{66}$	+ 70.0°		310°	0.781	
Pentatriacontane	$C_{35}H_{72}$	+ 74.7°		331°	0.781	
Octatriacontane	$C_{38}H_{78}$	+ 79.4°				
Hexacontane	$C_{60}H_{122}$	+102°				

The paraffins are not attacked by chlorine in the dark, nor do they absorb bromine or are they absorbed by sulphuric acid, and so can easily be separated from the other aliphatic hydrocarbons; they are hardly attacked at all by fuming nitric acid or by chromic acid in the cold. In daylight chlorine attacks them vigorously, giving substitution products, bromine less readily, and iodine has no action.

Detection and Estimation.—Fractional distillation at low temperatures may be applied to separate those hydrocarbons which are gaseous at ordinary temperature and pressure. Lebeau and Damiens (*Compt. rend.*, 1913, **156**, 144, 325) have shown that on cooling mixtures of methane, ethane, propane, iso-butane and hydrogen to the temperature of liquid air, methane has still a tension of 80 mm. of mercury, whilst the higher members are liquid. The gaseous portion is therefore methane and may be separated measured and analysed. The condensed portion is then successively fractionated from baths of solid carbon dioxide and acetone, and petroleum spirit cooled by liquid air, yielding binary mixtures of ethane and propane, propane and iso-butane, the components of which can be estimated by combustion Burrell and Robertson (*J. Ind. Eng Chem*, 1915, 7, 17, 112) describe a method by which the constituents of such complicated mixtures as coal gas can be accurately estimated in a practical way largely by the aid of fractional distillation.

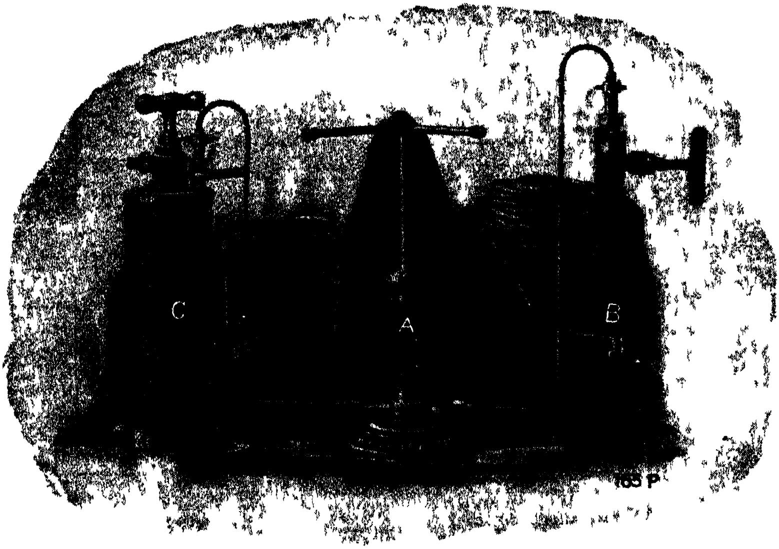

FIG 1 —Redwood s inflammable vapour and gas detector.

The detection of gaseous hydrocarbons in small quantities in admixture with air is of much practical importance, particularly methane or fire-damp in mine air, and petroleum vapours—which consist largely of hexanes—in the air of the holds and tanks of oil bearing vessels Methane forms an explosive mixture with air, the limits of inflammability varying according to conditions of temperature and pressure; under normal conditions the lower and upper limits of inflammability are about 6% and 15% respectively. The most delicate test for these gases or vapours is the hydrogen flame; when pure hydrogen is burned at a small jet in a non-explosive mixture of hydrocarbon gas and air a characteristic pale cap appears, under suitable optical conditions, above the hydrogen flame; the height of this cap is proportional to the amount of gas or vapour present. Using the Clowes-Redwood hydrogen lamp it is possible to detect and estimate as little as 0.2% of methane.

The apparatus (see Fig. 1) for this test is made by Messrs. Fraser and Co. Ltd., of Dagenham, Essex, England. It consists of the testing lamp (*A*) so constructed that when pure hydrogen from the cylinder (*B*) is burned at the jet and the suspected air or vapour from the sampling pump (*C*) is admitted into the chimney surrounding the jet, no flame can travel back to the mixture in the sampling pump. The chimney has a glass window in front for observation purposes; the size of the flame at the jet is so adjusted that its height is about ¼ inch, and it is just invisible to the eye of an observer placed level with the bottom of the window. The observer's head and the lamp are covered by a black cloth to exclude light and when the eye has become accustomed to the darkness the tap is so turned as to admit the suspected air slowly to the chimney. In the presence of any hydrocarbon vapour the flame cap appears at once, its height being proportional to the amount of such vapour. If the mixture is rich in hydrocarbons the hydrogen flame may be extinguished. It is essential for this test that the hydrogen shall be quite pure. In order to test the air in an enclosed place such as the hold of a ship, a pump is supplied with a length of flexible tubing. This tubing is lowered into the suspected place and the pump operated until the air in it is displaced and the barrel filled with the suspected air under pressure. The pump is then removed to the place of testing and connected with the hydrogen lamp. This test is applicable to all hydrocarbon gases and is also available for the detection of coal gas or of carbon monoxide.

The chemical estimation of methane in mine air or of other saturated hydrocarbons in a gaseous mixture is usually accomplished by combustion, since the paraffins are not readily absorbed by reagents. For the investigation of mine air, in which normally the amount of methane is less than the lower limit of inflammability, the most convenient apparatus is that of Haldane, a portable form of which is available for actual work in the mine. The usual types of gas analysis apparatus, such as those of Bone and Wheeler, Bunte, Orsat or Hempel, may also be used.

In Haldane's apparatus the combustion pipette consists of a bulb partly filled with mercury, above the surface of which is a small platinum spiral arranged so that it can be heated to bright redness by means of an electric current. On passing the gas or air, which obviously must contain an excess of oxygen, backwards and forwards over this red hot spiral for a few minutes the methane is completely oxidised to carbon dioxide and water. In the absence of other combustible gases the estimation of methane (or of ethane) is simple. The gas, after absorption of carbon dioxide in the usual way by potassium hydroxide solution, is oxidised in the combustion pipette, on cooling the water condenses and the carbon dioxide only remains. Consideration of the equations

$$CH_4 + 3O_2 \rightarrow CO_2 + 2H_2O \text{ and } 2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

shows that in the case of methane the contraction after the combustion is equal to twice the volume of methane: or in the case of ethane the contraction is 2.5 times the volume of the ethane. It is therefore only necessary to measure the volume of the gas before and after combustion, and from the contraction to calculate the quantity of methane or ethane. As a check on the accuracy the carbon dioxide produced in the combustion may be absorbed and measured. In the case of methane it is equal to the volume of methane oxidised, or the methane is one-third of the total diminution in volume after combustion and absorption by the potassium hydroxide solution. In the case of ethane the volume of carbon dioxide will be twice that of the hydrocarbon oxidised. Similar considerations may readily be applied to the higher paraffins.

For routine purposes the percentage of methane in mine air can be rapidly estimated without any preliminary absorption of carbon dioxide by simply measuring the volume contraction after combustion, one half of which is the methane content.

In the case of more complex mixtures, after the estimation of other gases by their appropriate absorbents, it may be necessary to estimate methane in the presence of other combustible gases such as hydrogen and carbon monoxide: several methods are available. The total combustible gases may be estimated by combustion by passing them, with excess of air or oxygen, through a heated platinum capillary tube such as that of Drehschmidt (*Ber.*, 1888, **21**, 3245) and subsequently absorbing the carbon dioxide by potassium hydroxide solution. By application of the stoichiometric equations the relative proportions by volume may be calculated. A more convenient method, however, is to absorb the carbon monoxide by means of ammoniacal solution of cuprous chloride; the methane and hydrogen are then passed over palladium-asbestos heated with a small burner so that the flame is only just coloured yellow by the glass, whereby the hydrogen is preferentially oxidised and the methane can be subsequently oxidised by the platinum spiral.

Mixtures of ethane and methane may be analysed by combustion, with the addition of air or oxygen if necessary; from the amount of carbon dioxide produced the relative proportions may be readily calculated. A chemical method for the detection of quantities of methane as small as 0.02 grm. has been devised by Hauser and Herzfeld (*Ber.*, 1915, **48**, 895); the methane is oxidised by ozone in the anode tube of a volt-ameter with a platinum electrode, whereby formaldehyde is produced which may readily be detected by the morphine and sulphuric acid reagent.

The separation of paraffins, whether liquid or gaseous, from hydrocarbons of the olefine or acetylene series is based upon the fact that when the mixture is heated in the dark with an excess of bromine, the paraffins are unaffected, whilst the unsaturated hydrocarbons are converted into liquid bromine compounds. The unchanged paraffins may be separated from the olefine bromides by distillation in a vacuum. A method, originally devised by Eldeleanu, which enables an approximate quantitative estimation to be made of paraffins in the presence of hydrocarbons of the aromatic series and of naphthenes, has been described by Engler and Ubbelohde (*Zeit. angew. Chem.*, 1913, **26**, i, 177). It depends upon the extraction of the aromatic and other unsaturated hydrocarbons from petroleum distillates by means of liquid sulphur dioxide at low temperature. At $-10°$ to $-18°$ aromatic hydrocarbons are soluble in all proportions of liquid sulphur dioxide (See Moore, Morell, and Egloff, *Met. and Chem. Eng.*, 1918, **18**, 396), naphthenes are partially soluble forming molecular complexes, and paraffins up to decane are insoluble. If a petroleum distillate is mixed with liquid sulphur dioxide, this is at first dissolved, but later two layers are formed, the lower one being a solution of hydrocarbons of high carbon content in sulphur dioxide, whilst some of the gas is dissolved in the upper layer of paraffins or naphthenes. A special burette is used having stopcocks at both ends which are prevented by clips from being forced out. The oil to be tested is cooled in the burette to −10°, liquid sulphur dioxide is then added (which by its own evaporation cools itself to the same temperature) until the two layers are just forming. One-third of the volume of the lower layer is added in excess, and the burette is then shaken and allowed to stand until separation is complete. The extract is run off, and the operation repeated twice with more sulphur dioxide. The bulk of the gas is allowed to evaporate in the air from both fractions and these are finally washed with water. No appreciable chemical action of the sulphur dioxide on the hydrocarbons takes place, but sulphur compounds are acted on. This method has the advantage over methods of nitration or sulphonation that the hydrocarbons are unchanged and may be recovered.

When paraffins are heated with bromine and water for some time in sunlight, they are converted into bromo-substitution compounds, half the bromine which enters into action being afterwards found as hydrobromic acid. This behaviour may, under favourable circumstances, be employed for their recognition and quantitative estimation.

Liquid paraffins may also be separated from hydrocarbons of other series by treating the mixture first with sulphuric acid, so long as the acid becomes coloured, and then with fuming nitric acid, avoiding rise of temperature. Other substances are oxidised, or converted into nitro- compounds which remain dissolved by the acids or are much less volatile than the unaltered paraffins. After washing with water, drying over potassium hydroxide and rectification over sodium, a distillate of pure paraffins is obtained.

Solid paraffins in a petroleum distillate may be estimated by a modification of the method originally proposed by Holde as follows: 100 grm. of the crude petroleum distillate are distilled up to 300°, the receiver is then changed, the thermometer removed, and the remainder of the oil distilled until only coke is left. Then 5 to 10 grm. of the oil are dissolved at room temperature in a mixture of equal parts of ethyl ether and absolute alcohol; the temperature is then lowered to −20° and more ether-alcohol added, so that all oily portions are kept in solution and only flakes of paraffin remain suspended. Oils containing much paraffin should be first dissolved in ether, the alcohol being added subsequently. The paraffin is filtered by suction on a funnel surrounded by a cooling mixture, washed with cooled ether-alcohol and then dissolved with hot benzene and, after evaporating the solvent and drying at 105°, weighed. In view of the not inappreciable solubility of paraffin in the ether-alcohol, a correction is made by adding to the result 0.2% for perfectly clear oils, 0.4% for semi-solid masses, and 1.0% for solid paraffins. It has also been shown that results so obtained are a little low on account of loss due to "cracking" in the distillation, but the figures have the merit of approximating very closely to those obtained in practice on the commercial scale. (Scheller, *Petroleum*, 1913, **8**, 905.)

It is frequently necessary to estimate conversely the amount of oil in a solid paraffin. Thus Marcusson (*Zeit. angew. Chem.*, 1910, **23**, 1057) bases the identification of a paraffin wax, according to its origin, upon the residual oil which it always contains. 100 grm. paraffin are dissolved in 300 c.c. of ethyl ether and the same volume of ethyl alcohol (96%) is then added; the mixture is cooled in running water and filtered on a Büchner funnel. The filtrate is evaporated again, dissolved in 50 c.c. of ether and precipitated with 50 c.c. of alcohol, cooled to −20°, filtered and evaporated. The iodine number is determined on the oily residue which may be taken up in benzine for further purification. This is from 3 to 12 with petroleum paraffins and from 18 to 21 with shale paraffins; but similar differences are observed before and after refining with samples of the same origin.

F. Sommer (*Petroleum*, 1912, **7**, 409) makes use of the formaldehyde method for the same purpose. 20 grm. of paraffin are melted in a flask, 20 c.c. of concentrated sulphuric acid are first added and then gradually 20 c.c. of formaldehyde solution, the flask being shaken and excessive heating avoided. The mixture becomes dark red and is left for 20 minutes on the water-bath; it is then turned into a porcelain basin and left on the water-bath until the paraffin is completely separated. After cooling, the paraffin cake is lifted off, the acid liquid is diluted with water, and the "formolite" is shaken out with chloroform. The chloroform solution is evaporated and the residue dried at 105°. The "formolite" varies from 0.02 to 1.55% and corresponds with the tendency of a paraffin to turn yellow.

F. Epstein and H. Polonyi (*Petroleum*, 1912, **7**, 594) employ the formation of picrates for the same purpose. 20 grm. of paraffin are melted at a low temperature, 0.02 grm. picric acid is added and well stirred in; after the insoluble matter has settled, the paraffin is poured into a mould of tinplate which floats on ice water. The colour of the solidified cake is compared with a standard sample, and 0.05% of oil in paraffin can thus be estimated.

For the removal of oxygen- and sulphur-containing asphaltic compounds from hydrocarbon oils Holde's (*Unters. der Kohlenwasserstofföle und Fette*, Berlin, 1913, p. 42) method is widely used. From 5 to 20 grm. oil are well shaken in a clear glass bottle with 40 volumes of "Normal" benzine (sp. gr. at 15° 0.695–0.705; boiling from 65° to 95°; free from unsaturated and benzene hydrocarbons). After standing for 24 hours at a temperature of from 15° to 20° protected from direct sunlight, the solution is filtered through a double filter and the residue washed with the same benzine until a drop of the filtrate leaves no oily residue on evaporation. The benzine solution then contains only the hydrocarbon oil. The asphaltic residue may be dissolved in coal tar benzene and, after evaporation of the latter, weighed (see p. 90).

By this method only the hard asphalt is removed. Soft asphalts can be separated by dissolving the oil in 25 volumes of ethyl ether and adding to the solution, drop by drop and with continual shaking, 12.5 volumes of 96% (by weight) alcohol. After 5 hours' standing the precipitate is filtered and washed with a mixture of ether and alcohol in the same proportions (1:2) until 20 c.c. of the filtrate leave on evaporation no oily residue but only traces of a pitchy substance. The precipitate is dissolved in benzene and, after evaporation of the latter, weighed. If it is light in colour and likely to contain paraffin wax, this is separated by treatment with absolute alcohol in an extracting apparatus, preferably after mixing it with sand or alcohol extracted charcoal.

F. Schwarz (*Chem. Zeit.*, 1911, **35**, 1417) uses butanone (methyl-ethyl-ketone) which has been saturated with water, in which hydrocarbon oils are soluble and asphaltic substances insoluble, in the place of either of the two preceding reagents, thereby obtaining hard and brittle asphalt residues (for details see page 209).

OLEFINES

This class of hydrocarbons shares with the polymethylenes the general formulæ C_nH_{2n}; its members closely resemble the paraffins, into which they are converted by nascent hydrogen, in physical properties. Containing as they do less hydrogen than the paraffins, they are unsaturated compounds and hence unite very readily with bromine, even in the dark, and with halogen acids or concentrated sulphuric acid. The boiling points of the olefines are close to those of the paraffins of similar constitution containing the same number of carbon atoms and their melting points slightly lower. Some of the physical properties of the normal olefines are as follows:

	FORMULA	M. P.	B. P.	SP. GR.
Ethylene	C_2H_4	$-160°$	$-103°$	0.978 } air = 1
Propylene	C_3H_6	.....	$-50°$	1.498
Butylene	C_4H_8	.....	2°	....
Amylene	C_5H_{10}	.....	39°	0.678 at 15°
Hexylene	C_6H_{12}	$-99°$	68°	0.685 at 15°
Heptylene	C_7H_{14}	.....	99°	0.705 at 15°
Octylene	C_8H_{16}	.....	124°	....
Nonylene	C_9H_{18}	....	153°	....
Decylene	$C_{10}H_{20}$	.....	172°	0.763 at 0°

Detection and Estimation of Olefines.—The only methods practically available for the direct and accurate estimation of olefines, when in admixture with hydrocarbons of other series, are based on the facility with which they unite with bromine, or their absorption by fuming sulphuric acid.

For the estimation of the *gaseous olefines*, as existing in coal-gas, a known measure of the gas is introduced into a graduated Cooper's tube, care being taken that the water which is displaced has been previously saturated with gas of the same quality. Bromine is then dropped into the water which remains in the curved part of the tube, the tube closed with a stopper or the thumb, and the contents well agitated. On opening the tube under water, the diminution of the volume of the gas will indicate that olefines have been absorbed, and, on observing the water, oily globules of $C_2H_4Br_2$ etc., will be perceived. These should be red or yellow in colour; if colourless, more bromine must be added and the agitation repeated. The tube being again opened under water, a small piece of sodium hydroxide is added to absorb free bromine, and the tube agitated once more. The tube is then immersed in a cistern having glass sides, so that the volume of the residual gas can be read off when the water in the cistern is on the same level with that in the tube. The loss of volume, duly corrected, if necessary, for temperature and pressure, gives the hydrocarbons absorbable by bromine. In gas mixtures containing ethylene (or propylene) acetylene and benzene the ethylene or propylene may be estimated (Treadwell and Tauber, *Helv. Chim. Acta.*, 1919, **2**, 601.) by shaking the gas for one or two minutes with 5 c.c. of a solution containing 20 grm. of mercuric cyanide in 100 c.c. of 2N sodium hydroxide solution; this absorbs the acetylene only. The residual gas is then shaken for about 3 minutes with 5 c.c. of a solution of 20 grm. of mercuric nitrate in 100 c.c. of 2N nitric acid saturated with sodium nitrate, which solution absorbs the ethylene or propylene only, the remaining benzene can then be measured.

Satisfactory estimations of olefines can also be made by means of Hempel's gas-burette or Lunge's nitrometer. The sulphuric acid method is the more accurate, and absorption is much more rapid if 1 grm. of vanadic anhydride or 6 grm. of vanadyl sulphate is dissolved in each 100 grm. of the sulphuric acid, which should be of sp. gr. 1.84. Such acid will rapidly absorb 150 times its volume of ethylene (Lebeau and Damiens, *Compt. rend.*, 1913, **156**, 557). When the gas mixture is shaken in the burette with this solution the diminution in volume indicates the amount of the unsaturated hydrocarbons. When the proportion of olefines is small a known volume of the gas may be bubbled slowly through a solution of bromine in carbon disulphide.

An approximate method for the estimation of the unsaturated aliphatic or hydro-aromatic hydrocarbons in general in the liquid state consists in shaking the mixture repeatedly with 10% to 30% by volume of concentrated sulphuric acid until the volume shows no further reduction.[1] The loss then indicates the percentage of unsaturated compounds. Heating must be avoided and, if aromatic or naphthene hydrocarbons are present, the acid must be added very carefully to avoid a violent action, as these are sulphonated at high temperature by concentrated, and even at slightly raised temperature by fuming sulphuric acid.

A qualitative test for olefines by means of mercuric acetate has been devised by Balbiano and Paolini (*Chem. Zeit.*, 1901, **25**, 932; *Ber.*, 1902, **35**, 2994; see also K. A. Hofmann and J. Sand, *Ber.*, 1900, **33**, 1340, 1353; 1901, **34**, 2906; Denigès, *Bull. Soc. chim.*, 1898 [3], **19**, 494). 3 to 4 c.c. of a hydrocarbon mixture are shaken with 10 c.c. of a saturated solution of this salt. If olefines are present a deposit of white crystals will be observed after 24 hours.

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[1] Note.—The estimation of liquid olefines by sulphuric acid is not altogether satisfactory on account of polymerisation which takes place with olefines of higher molecular weight; see Brooks and Humphrey, *J. Amer. Chem. Soc.*, 1918, **40**, 822.

Tausz and Wolf (*Zeit. angew, Chem.*, 1919, **32**, 317) base a method for the estimation of the olefines on this behaviour. Thus for the analysis of a liquid hydrocarbon mixture, such as petroleum spirit, 30 grm. of mercuric acetate are dissolved in 500 c.c. of water and introduced into a special flask with 15 c.c. of alcohol and 50 c.c. of the sample. The mixture is then heated on a strongly boiling water-bath under a reflux condenser for 8 hours. The flask has a side tube so arranged that it may be connected with a well cooled reflux condenser for the boiling and then may, by reclining it, be connected with a vertical condenser for the distillation. It is advisable to cool the condenser with alcohol and carbon dioxide both when refluxing and when distilling. After the 8 hours those hydrocarbons which have not reacted are distilled off in a current of steam. The distillate is washed with dilute acetic acid, then with sodium bisulphite solution, and the residual saturated hydrocarbons are measured. A constant 1.05% is added to compensate for the loss in the apparatus. The combined unsaturated hydrocarbons are now liberated by pouring hydrochloric acid into the flask and the contents are steam-distilled as before.

The bromine method used for the estimation of the gaseous olefines has also extensive application to the analysis of liquid hydrocarbons. Unsaturated aliphatic hydrocarbons and aromatic hydrocarbons (also phenols and a number of other substances if present) will absorb bromine, but in the case of aromatic compounds there is the formation, not of olefine bromides, but of substitution products with the elimination of a corresponding quantity of hydrogen bromide. The method was originally described by Mills and Snodgrass but has since been modified by other investigators. The bromine and the hydrocarbon mixture are usually dissolved in carbon tetrachloride, and, as has been pointed out by McArthur, the amount of bromine added must be about twice the quantity (ascertained by a preliminary experiment) required for the absorption. Water should be rigorously excluded. It is also necessary that the hydrocarbon should not be exposed to the action of the bromine in strong light: even a moderately diffused daylight is prejudicial, but gas light has no sensible effect. About 15 minutes should be allowed for the bromination, if this time be much exceeded secondary changes are liable to occur which give rise to results in excess of the truth.

In order to distinguish between added and substituted bromine which will both be covered by the bromine absorption of, say, a mixture of olefines and aromatic hydrocarbons, McIlhiney (*J. Amer. Chem. Soc.*, 1899, **21**, 1084) estimates the hydrogen bromide formed in the latter case.

The sample is dissolved in 10 c.c. of carbon tetrachloride in a glass-stoppered bottle and 20 c.c. of N/3-bromine solution in the same solvent are added. After a few minutes 20 to 30 c.c. of a 10% solution of potassium iodide are added, care being taken that no bromine is lost; if necessary the mixture must be cooled and the stopper and neck of the bottle wetted with potassium iodide solution. The bottle is then shaken to ensure the absorption of the bromine and hydrogen bromide by the aqueous solution. The iodine present is now titrated with N/10-sodium thiosulphate. By then adding 5 c.c. of a neutral 2% solution of potassium iodate, a quantity of iodine equivalent to the hydrogen bromide formed is liberated and, on titrating this, the bromine solution figure may be calculated. All solutions should be tested for acidity and a blank test made. Whilst addition of bromine is instantaneous, the amount of substitution is somewhat affected by the time of contact. The bromine calculated from the hydrogen bromide, and expressed as bromine per 100 grm. of the sample, gives the substituted bromine value, and twice this figure deducted from the total bromine absorption gives the bromine addition value, which is a measure of the unsaturated hydrocarbons present.

Owing to the complex character of commercial hydrocarbons, an estimation of the amount of bromine combining with them does not always give the means of calculating the percentage of olefines present. If, however, a fraction of constant b. p. be prepared and its vapour density ascertained, its mean combining weight can be deduced, and an estimation of its power of assimilating bromine gives a means of obtaining a close approximation to the proportion of olefines contained in the fraction. This suggested method assumes that the fraction consists essentially of paraffins and olefines. A mixture with hydrocarbons of other series would further complicate the problem.

When the hydrocarbons present are known a useful method of estimation by bromine absorption, which has been worked out by Routala (*Ann. Acad. Sci. Fennicae*, 1912, A, **2**, 19, c.f. Analyst, 1912, **37**, 462) may be applied. This process is applicable to hydrocarbon oils, and for checking the purity of commercial ethylenic preparations. The bromine value (in grm. per 100 grm. of sample) is determined by Frank's method and the olefine percentage (A) is calculated from the bromine value (B) by the formula $A = [K + (n - 5)c]B$ where n is the number of carbon atoms and K and c are constants calculated for each hydrocarbon so that $\frac{\%\text{ of ethylene}}{\text{bromine value}}$ is a constant. K is 0.4375 for amylene, 0.595 for hexylene 0.6075 for heptylene, and for each increment of CH_2 the constant increases on the average $0.0875 = c$.

The bromine absorption may serve not only for the estimation but also for the removal of unsaturated from saturated hydrocarbons, which can be separated by distillation from the higher-boiling bromo-compounds.

Sometimes the iodine number is determined in preference to the bromine absorption. For this purpose the employment of Wijs' (*cf.* Vol. II, p. 35) method is advisable and preferable to that of Hübl. In the case of crude distillates it is necessary to remove any hydrogen sulphide that may be present by shaking with a solution of lead acetate. (Graefe, *Zeit. angew. Chem.*, 1905, **18,** 1580.

Frank (F. Frank, *Die Chem. Ind.*, 1901, **24,** 263) in his method, which was originally devised for the estimation of the unsaturated hydrocarbons in commercial benzol, employs an aqueous solution of potassium bromide and bromate which, when acidified, liberates bromine equivalent to a N/10 solution. This standard solution contains 9.9167 grm. of potassium bromide and 2.7833 grm. of potassium bromate in 1000 c.c. For the estimation of the bromine absorption 5 c.c. of the oil or hydrocarbon are added to 10 c.c. of dilute sulphuric acid (1:5) in a stoppered flask and the bromide-bromate solution is run in from a burette until the red colour of the bromine in the upper layer persists after five minutes' shaking and, after standing for 15 minutes, there is still excess of bromine indicated by a drop of the liquid placed upon a piece of starch-iodide paper. The result is calculated in terms of the percentage of bromine absorbed; each c.c. of the bromide-bromate solution is equivalent to 0.008 grm. of bromine. Under the conditions of the experiment the aromatic hydrocarbons only absorb negligible quantities of bromine.

THE ACETYLENES

The members of this group have the general formulæ C_nH_{2n-2}. The first two members, acetylene and alleylene, are gaseous, the higher ones are usually oily liquids of rather higher b. p. than the corresponding paraffins; they are, of course, unsaturated compounds, containing a triple linkage, and react with hydrogen, the acids, halogens, etc., in very much the same manner as the olefines. Their most characteristic property is the great readiness which with they react with ammoniacal solutions of cuprous or silver salts, forming compounds, such as $C_2H_2.Cu_2O$, which are almost always thrown down as precipitates. By this property they can be distinguished and separated from all other hydrocarbons.

The cuprous solution is prepared by treating copper turnings in a separator with strong ammonia in presence of a limited quantity of air, until the blue liquid first formed has become colourless. The reagent is then run from the tap into a U-tube fitted with a tube bent twice at right angles, the open end of which dips under water, so as to prevent contact of air. On passing a gas through the cuprous solution, a yellow or red precipitate will be produced if acetylenes be present. If the precipitate be filtered from the liquid and treated with strong hydrochloric acid, the acetylene will be liberated. This behaviour furnishes a means of isolating acetylene and its homologues in a condition of purity. On treating the cuprous compound with aqueous ammonia and zinc, the corresponding olefine will be produced, and may be identified by the proportion of bromine with which it unites.

The silver derivatives of the acetylenes may be obtained by substituting an ammoniacal solution of silver nitrate for the cuprous solution. A solution prepared by dissolving cuprous or silver chloride in ammonium hydroxide *absorbs* acetylenes, but some of the hydrocarbons are not *precipitated* by such a reagent, as their metallic derivatives are soluble in ammonium hydroxide containing ammonium chloride.

Acetylene, C_2H_2, is an important illuminating agent. It may be prepared in various ways, but the only one of moment is the action of water on calcium carbide, by which calcium hydroxide and acetylene are the only products. Acetylene is a colourless gas with a faint ethereal odour; it is usually regarded as highly poisonous, but several investigators deny this. As prepared from commercial calcium carbide it is very impure, and the disagreeable odour and poisonous action attributed to the acetylene itself are due to the impurities, especially hydrogen phosphides and sulphur compounds.

Water dissolves about 1.1 times its volume, but a saturated solution of common salt dissolves only about 0.05 volume. Alcohol dissolves about 6 volumes and paraffin about 2.5; acetone or acetaldehyde (J. H. James, *J. Ind. Eng. Chem.*, 1913, **5**, 115) dissolves a large amount, especially under pressure. Large quantities of acetylene are sold for welding, cutting or lighting purposes compressed into cylinders containing acetone and a porous agglomerate of asbestos and charcoal, or a charcoal filling.[1] Since the density of acetylene is nearly that of air, it diffuses slowly; hence the danger of formation of explosive mixtures in the neighbourhood of a leak. The lower limit of inflammability when mixed with air is 2.5%, and the most violent explosion is produced by a mixture containing 8.37% by volume of the gas. Acetylene is liquefied at 0° by a pressure of 21.5 atmospheres; at 20° by a pressure of 42.8 atmospheres. The critical temperature is 37.05° at 68 atmospheres.

Liquid acetylene has a sp. gr. of 0.4 and is highly expansible. It is liable to explosive dissociation, and the conditions under which this occurs have been extensively studied. Berthelot and Vieille placed 18 grm. of acetylene in a small flask and fired the mass by means of a wire rendered incandescent by an electric current. The pressure rose to 5638 atmospheres, and the carbon was left as a lump with brilliant surface and conchoidal fracture. Explosion may also be brought about by fulminating powder and even by friction. The presence of hydrogen phosphide, which is spontaneously inflammable, is said to have been the cause of at least one explosion.

On heating acetylene undergoes a variety of condensations, many of which are of industrial importance. (See Pyrogenesis of hydrocarbons. *J. Ind. Eng. Chem.*, 1917, 879, 88 and *J. Inst. Petrol. Tech.*, **3**, 36.)

Detection and Estimation.—Acetylene can be estimated by titrating the free nitric acid produced by the action of the gas on a solution of silver nitrate (Chevastelon, *Compt. rend.*, 1897, **125**, 245). The change is represented as follows:

$$C_2H_2 + 3AgNO_3 = C_2Ag_2.AgNO_3 + 2HNO_3.$$

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[1] For particulars of these fillings see, *Home Office Report on Storage of Dissolved Acetylene*, London, 1918.

The mixture must not contain any gases which interact with nitric acid or which are themselves acid in character, and the silver nitrate must be in excess. The only data necessary for the calculation are the volume, temperature, and pressure of the gas, and the final volume and acidity of the liquid. The operation may be performed in a Raoult eudiometer, 20 c.c. of a 10% solution of silver nitrate sufficing for a 60 c.c. eudiometer, distilled water being afterwards run in until the pressure is equalised.

In gaseous mixtures containing up to about 12% by volume of acetylene it may be estimated by precipitation as cuprous acetylide as described by J. A. Muller (*Bull. Soc. Chem.*, 1920, **27**, 69). The reagent is an ammonical cuprous chloride solution prepared by adding 1.2 to 1.3 grm. of cuprous chloride in 50% solution to 6 c.c. of strong ammonia solution with 5 c.c. of water. This solution is shaken in a flask with 70 to 80 c.c. of the gas mixture until the acetylene is completely precipitated. The flask is nearly filled with 10% brine and the liquid acidified with acetic acid; the precipitate is then filtered off, washed and treated on a crucible with strong sulphuric acid until a homogeneous mass is obtained which is heated until all the excess of acid is driven off. The crucible is next ignited and the precipitated copper weighed as CuO. The weight of CuO × 0.1407 gives the volume in c.c. of acetylene.

A method for the estimation of acetylene in the presence of olefines has been given on page 14. A colorimetric method suitable for the detection and estimation of minute quantities of acetylene as small as 0.001 c.c. is given by Schulze (*Zeit. angew. Chem.*, 1916, **29**, 341; see also Weaver, *J. Amer. Chem. Soc.*, 1916, **38**, 352), and is based upon the colour produced by passing air containing the acetylene through Ilosvay's ammoniacal cuprous chloride solution to which gelatin has been added to prevent the precipitation of cuprous acetylide. The colour produced is matched against a similar quantity of solution through which air containing 1% of acetylene has been passed.

The most serious impurity of acetylene, as prepared by the action of water on commercial calcium carbide, is hydrogen phosphide, which, like ammonia, appears to favour the formation of the explosive copper acetylide, and, if present in notable quantity, may render the gas spontaneously inflammable. Sulphuretted hydrogen also is commonly present in acetylene prepared from calcium carbide.

The purity of acetylene and of the carbide from which it is prepared are the subject of regulations[1] by the British Acetylene and Welding Association and by the German and Austrian Acetylene Unions. The British standard for the purity of the gas is that it shall not contain more than the following proportions by volume of impurities, *viz.*:

Phosphoretted hydrogen PH_3	0.05%
Sulphuretted hydrogen SH_2	0.15%

For the estimation of the hydrogen phosphide, hydrogen sulphide and the volume of gas yielded by the carbide the following process,

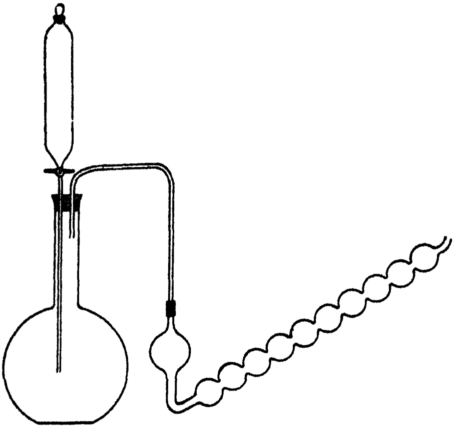

FIG. 2.

which is a modification of the original process of Lunge and Cedercreutz (*Zeit. ang. Chem.*, 1897, **10**, 651), is prescribed by the Association. For the estimation of phosphorus and sulphur the carbide is broken and about 100 grm. weight of lumps about the size of peas and free from dust is put into a half-litre flask with a rubber cork tap funnel and gas outlet. The gas outlet is connected by a short piece of rubber tubing with a ten bulb absorption tube (see Fig. 2) previously charged with 150 c.c. of a 2.5% solution of sodium hypochlorite, which must be free from sulphate and phosphate. The outlet of the absorption tube is connected by rubber tubing with the inlet of an experimental meter by which the yield of gas is measured. If the yield of gas is being estimated otherwise, the experimental meter may be dispensed with in this test. The tap funnel, which should have a high cylindrical body is filled with water, and the tap is turned to admit three to five drops per minute to the flask. When the evolution of the gas slackens, the rate of admission of the water may be increased, but the decomposition of the carbide should extend over at least two hours at a uniform rate, otherwise absorption of the hydrogen phosphide by the sodium hypochlorite will be incomplete. The carbide residue is finally completely submerged by water admitted through the tap funnel. Coal gas or air is drawn through the flask and absorption tube to displace the residual acetylene, and the contents of the absorption tube are washed out into a beaker. Dilute hydrochloric acid is added and the liquid boiled until all the chlorine is expelled, and the solution is then filtered. The filtrate is made up to a known volume, one half of which is taken for the estimation of phosphorus by adding ammonia and magnesium mixture in the usual way. The sulphate in the other half of the solution is precipitated by means of barium chloride. From the weights of magnesium pyrophosphate and of barium sulphate the amounts of hydrogen phosphide and sulphide are calculated.

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[1] Regulations dated Jan. 1, 1923. Obtainable from the offices of the Association at 38 Victoria St., London, S. W.

In the estimation of the volume of the gas no correction is applied for the tension of aqueous vapour.

Methods of analysis are also published by the German Acetylene Union.

It may be remarked that the amount of hydrogen sulphide in different specimens of acetylene yielded by the same calcium carbide varies considerably, according to the conditions obtaining at the time of preparation. Moreover, the whole of the sulphur in the gas does not exist as hydrogen sulphide.

P. W. Wolff (*Chem. Zeit.*, 1898, **22**, 281) and Keppeler (*J. Gasbeleucht* 1904, **47**, 62) show that the employment of hypochlorites for removal of hydrogen phosphides, will involve danger when notable amounts of ammonia are present, in consequence of the formation of nitrogen chloride. The ammonia should be first removed by thorough washing. Chlorine and moisture may be removed by subsequent treatment with lime. Acetylene thus purified has a faint ethereal odour, and does not attack copper or copper alloys. The stains on copper fittings when common acetylene is used are due to copper phosphide.

Lewes (*J. Gas Lighting*, Nov. 30, 1897) states that acetylene is much safer when diluted with other combustible gases. The best diluent is a mixture of 30% methane with hydrogen or carbon monoxide, or both. This diluting gas when mixed with 10% of acetylene is a convenient substitute for coal-gas.

Hempel and Kahl (*Zeit. angew. Chem.*, 1898, **11**, 53) suggest a volumetric method for estimating hydrogen phosphide in acetylene. A solution of 15.6 grm. of copper sulphate ($CuSO_4, 5H_2O$) in 100 c.c. of water, to which were added 5 c.c. of dilute sulphuric acid (1 volume of concentrated acid to 4 volumes of water), was found to be the best absorbent. One c.c. of the solution absorbed 8.8. c.c. of hydrogen phosphide and 0.2 c.c. of acetylene from 100 c.c. of each gas. In the presence of mercury and excess of the solution of copper sulphate, the diminution of volume resulting from the absorption of hydrogen phosphide exactly corresponded to four times the volume present. Hydrogen phosphide produced by heating an alcoholic solution of potassium hydroxide with ordinary phosphorus was mixed in various known proportions with nitrogen, and the phosphide determined. The mean value was 52.4 per cent., and mixtures of known volumes of this mixture and acetylene were examined by agitating it for three minutes, in a pipette sealed with mercury, with 3 c.c. of the copper sulphate solution. It was assumed that the hydrogen phosphide amounted to ¼ of the diminution of volume. The test analyses were satisfactory.

Detection of Acetylene in Cases of Poisoning.—D. Vitali (L'Orosi, 1898, **21**, 217) recommends the following method: A sample of blood is mixed with 5 or 8 % of pure dry acetone, placed in a retort, and distilled into an empty condenser and a set of absorbing bulbs containing more acetone. The retort is heated on a water-bath, and the condenser and bulbs kept cold in ice. The acetone passes over, carrying the acetylene with it, and the latter may be identified by its characteristic reactions. Hydrogen sulphide and phosphide, which occur in the crude gas, also dissolve in the acetone, and can be sought for therein.

Calcium carbide is prepared by the action of an electric current upon a mixture of quicklime and carbon (coke or anthracite coal). Pure calcium carbide is brown, but the commercial form is a hard, grayish, slag-like mass, which, when exposed to the air, usually emits an odour of hydrogen phosphide, and slowly crumbles to a dry powder. It is often irregular in quality. A considerable proportion of free carbon may often be observed in it, and great care must be taken in sampling. Water acts violently on calcium carbide, but a strong aqueous solution of zinc chloride acts much more slowly. Calcium carbide may be used for the detection and estimation of water in alcohol, since absolute alcohol is without action upon it.

The regulations of the British Acetylene and Welding Association already referred to prescribe methods to be employed for the sampling of carbide, and standards of size as well as gas yields. The following paragraphs are extracted from these regulations.

Carbide of calcium shall be deemed to be broken or crushed and sorted in accordance with the following sizes which shall be determined by screening: the carbide being retained by a sieve having mesh holes of the first size indicated and passing through a sieve having mesh holes of the second size indicated, *viz.:*—1–2 mm.; 2–4 mm.; 4–7 mm.; 7–15 mm.; 15–25 mm.; 25–50 mm.: 50–80 mm.; 80–120 mm. It shall be guaranteed to yield, under the test conditions already described, not less than 4.8 cubic feet of acetylene per pound of carbide, less 5% margin for possible inequalities in sampling or loss in analysis, except that a further allowance shall be made for loss of gas in breaking and packing the carbide of less than 15–25 mm. size, *viz.:* for size 7–15 mm. 5% allowance; for size 4–7 mm. 10% allowance; for size 2–4 mm. 15% allowance and for size 1–2 mm. 20% allowance.

The effect of these allowances is as follows: Standard guaranteed yield of 4.8 cubic feet per pound less 5% for inequalities.

Net gas yield for all sizes from 15 mm. to 20 mm.	4.56 cu. ft.
Net gas yield for all sizes from size 7–15 mm	4.32 cu. ft.
Net gas yield for all sizes from size 4–7 mm	4.08 cu. ft.
Net gas yield for all sizes from size 2–4 mm	3.84 cu. ft.
Net gas yield for all sizes from size 1–2 mm	3.60 cu. ft.

AROMATIC HYDROCARBONS

In contrast with the open-chain compounds already described, the Cyclic or Aromatic hydrocarbons, which contain a larger percentage of carbon in their molecule, have some or all of their carbon atoms in the form of a closed chain or ring. This nucleus is in general of relatively great stability, and the cyclic hydrocarbons cannot therefore—with the exception of the polymethylenes—be transformed into simpler hydrocarbons, as the nucleus undergoes oxidation with difficulty, giving rise to simple organic acids. They differ materially from the members of the acyclic series in their behaviour with nitric acid; the lower members of the paraffin series do not react at all with nitric acid, although low yields of nitroparaffins are obtainable from hexane and the higher members. The aromatic hydrocarbons on the other hand, readily yield characteristic nitro-derivatives. In a similar way sulphuric acid forms sulphonic acids with the benzene series, a type of reaction quite peculiar to cyclic compounds. The homologues of benzene differ from the paraffins also in the ease with which the side chain is oxidised with the production of benzene-carboxylic acids. With halogens two types of reaction take place—addition and substitution, the latter being more usual and more important.

General Methods Applicable to Aromatic Hydrocarbons

Mention has already been made of the sulphonation of aromatic hydrocarbons by heating them with concentrated or fuming sulphuric acid. From the sulphonic acids thus produced, or separated from mixtures, the hydrocarbon may be recovered by distillation with superheated steam.

A more generally useful method by which these hydrocarbons may be recognised and isolated from mixtures is nitration. The carefully fractionated hydrocarbons are treated with 2 to 5 times their volume of a nitrating mixture consisting of 1 volume of nitric acid (sp. gr. 1.45–1.50) and 1.5 to 2 volumes of sulphuric acid (sp. gr. 1.85). With good stirring or shaking, careful mixing and low temperature, mostly mono- and di-nitro-products are formed. At higher temperature, or with great excess of acid, tri-nitro-compounds will be formed.

When no further action takes place the nitration is completed, and the mixture then separates into 3 layers. The acids form the bottom layer, the nitro-compounds are in the dark-brown middle layer, and the unattacked hydrocarbons in the upper layer. The two upper layers are soluble in each other to a certain extent. The acids are either separated first or after dilution with water. The hydrocarbons and nitro-products are washed with water and a little sodium carbonate solution, and are separated by distillation, with or without steam. The nitro-compounds, if solid, can be identified by their melting points, or else by reduction to their amines and possibly the conversion of the latter into acyl derivatives or salts.

Formaldehyde also is a reagent of fairly general applicability in hydrocarbon analysis, and was suggested for this purpose by A. Nastjukoff in 1904. (*J. Russ. Chem. Phys. Soc.*, 1904, **36,** 881; 1910, **42,** 1596.) He found that a mixture of concentrated sulphuric acid and formaldehyde solution reacts with all unsaturated cyclic hydrocarbons forming insoluble compounds, termed "formolite." Neither saturated hydrocarbons of any kind nor unsaturated chain hydrocarbons show this behaviour, but all aromatic and partially saturated hydro-aromatic hydrocarbons, as well as terpenes and hydroterpenes, yield "formolites."

The sample is mixed with its own volume of concentrated sulphuric acid, and half its volume of a 40% formaldehyde solution is then slowly added, the mixture being well cooled the whole time. (If the yield of "formolite" is higher than 50%, the ratios of sample, sulphuric acid and formaldehyde to be taken are 1:2:1.) It is then shaken until the temperature no longer rises. In many cases, particularly with viscous oils, it is advisable to dilute the sample previously with light petroleum spirit free from "formolite"—yielding hydrocarbons. After half an hour's standing, the mixture is poured into ice water, the flask being washed out with water. An excess of ammonia is added to the acid solution, and the precipitate is filtered off and washed on a vacuum filter. The precipitate from heavy oils is first washed with petroleum spirit to remove unattacked oil, then with water until free from ammonia, and is then dried at 105°. In view of the difficulty of filtration and washing, it is sometimes necessary to repeat the extraction of the dried and powdered precipitate with petroleum spirit and water.

Nastjukoff calls the number of grm. of precipitate per 100 c.c. of original oil the "formolite number" of the oil or hydrocarbon mixture. The precipitates are of a yellow to brown color and are practically insoluble in the usual solvents, except to a small extent in chloroform.

The composition of the "formolites" is not yet cleared up; the unsaturated cyclic hydrocarbon combined with the formaldehyde is equal to about 80% of the "formolite." It has been proposed by V. F. Herr (*Chem. Zeit.* 1910, **34**, 893) to use methylal in place of formaldehyde on account of its solvent power for oils, and Radcliffe (*Pert. Ess. Oil. Rec.*, 1920, **11**, 48) shows that this reagent enables as little as 1% of benzol to be detected in a light petroleum.

THE BENZENE SERIES

These hydrocarbons have the general formula C_nH_{2n-6}. All the members except the first two, benzene and toluene, exist in several isomeric forms. They are mainly derived from coal tar and will be dealt with at length in Vol. VI.

POLYNUCLEAR HYDROCARBONS

This group, which contains a large number of compounds of industrial importance, is characterised by the fact that one or more of the carbon atoms of the benzene nucleus participate in the formation of other carbocyclic rings. The more important members indene, naphthalene, anthracene, phenanthrene, fluoranthene, pyrene etc. are considered fully in other sections.

NAPHTHENES (POLYMETHYLENES)

These hydrocarbons have the general formula C_nH_{2n} and are thus isomeric with the olefines. After removal of the unsaturated aliphatic and the aromatic hydrocarbons from a mixture, the polymethylenes and paraffins remain. Their separation is particularly difficult on account of the similarity of their physical and chemical characteristics. Specific gravity and refractivity will give some indication for their differentiation; generally, qualitative tests will meet the case.

PHYSICAL PROPERTIES OF THE SIMPLEST CYCLOPARAFFINS[1]

Name	M. p.	B. p.	Sp. gr. at 4°	n_D^{20}
Cyclopropane (trimethylene)..... C_3H_6	−126.0°	about −35°	......	....
Cyclobutane (tetramethylene).. . C_4H_8	liquid at −80°	11.0–12 0°	0.7038	1.37520
Cyclopentane (pentamethylene) . C_5H_{10}	liquid at −80°	49°	0.7635	1.40855
Cyclohexane (hexamethylene). . . C_6H_{12}	+ 6.4°	81°	0.7934	1.4266
Cycloheptane (heptamethylene). . C_7H_{14}	....	117.0–117.5°	0.8252	1.44521
Cyclooctane (octamethylene)... . C_8H_{16}	+11.5°	145.3–148.0°	0.850	1.45777
Cyclononane............ .. . . C_9H_{18}	....	170.0–172.0°	0.785	1.4328

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[1] R. Willstätter and J. Bruce, *Ber.*, 1907, **40**, 3981.

Hydrocarbons of the polymethylene series are not attacked by a mixture of sulphuric and nitric acids at the ordinary temperature, nor readily on moderate heating (Francis and Young, *Trans.*, 1898, **73**, 928). With fuming nitric acid the behaviour of pentamethylene and hexamethylene differs widely from that of their methyl derivatives, for the former are only attacked when heated and yield chiefly the corresponding dibasic acids—glutaric and adipic acids—whilst the methyl derivatives and especially methylpentamethylene, are acted on rapidly at the ordinary temperature with evolution of heat and are for the most part broken down (Radcliffe, *Pert. Ess. Oil. Rec.*, 1920, **11**, 48).

If heated with dilute nitric acid in sealed-tubes, the polymethylenes yield according to Konowaloff (*Ber.*, 1895, **28**, 1863; *Chem. Zentr.*, 1898, i, 926; 1899, i, 966; 1902, i, 564) mono-nitro-compounds which are of tertiary character if the original hydrocarbon has a side chain. 5 c.c. of the hydrocarbon are heated in a sealed tube with 25 c.c. of nitric acid of sp. gr. 1.025 to 1.075 for 12 hours at 120° to 130°. The product is washed with sodium carbonate solution and water and dried with calcium chloride. The unattacked hydrocarbon is distilled off. If the distillation is carried out under reduced pressure, it can be continued until the nitro-compounds are carried over. Secondary nitro-compounds are separated from the tertiary by extraction of the mixture with alcoholic or dilute aqueous potassium hydroxide.

Polymethylenes may be qualitatively tested by de-hydrogenating them according to Sabatier's method. Cyclohexanes are converted into aromatic hydrocarbons by passing them over finely divided and freshly reduced nickel at 300° and can then be easily identified by the formol reaction.

Zelinsky (*Ber.*, 1911, **44**, 3121) converted *cyclo*hexane quantitatively into benzene and hydrogen by passing it 3 times very slowly over palladium black at 300°.

In this connection mention may be made of S. Fokin's (*Russ. Phys. Chem. Soc.*, 1908, **40**, 700) proposal to estimate the degree of unsaturation of organic compounds by the determination of the "hydrogen number," *i. e.*, the number of c.c. of hydrogen (at 0° and 760 mm.) which are absorbed by 1 grm. of the substance when submitted to hydrogenation. A distillation flask (50 to 150 c.c.) having a small beaker fused inside on the bottom is connected by means of the side tube with a gas burette and a gas holder containing hydrogen. In the small beaker are placed 0.1 to 0.2 grm.

of molecular platinum moistened with 0.25 to 0.5 c.c. of water, and in the flask the substance to be examined and 20 to 30 c.c. of alcohol free from dissolved oxygen. The flask is shaken by a shaking machine and the hydrogen absorbed is read off when constancy is obtained.

Willstätter (*Loc. cit.*) had previously hydrogenated polymethylenes by means of Sabatier and Senderens' method.

A method for the estimation of the total hydrogen contained in a substance is due to A. P. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 195, 208; *Zeitsch. anal. Chem.*, 1907, **46**, 357). From 0.25 to 0.5 grm. of the substance is mixed with about 1 grm. of powdered magnesium, which has been ignited previously in a current of hydrogen and the mixture is introduced into a thick-walled test-tube made out of combustion tubing. This tube should be 130 mm. long and 9 mm. in diameter, a layer of magnesium powder is placed above the mixture so as to fill the tube to a height of about 80 mm. After connecting the open end of the tube with a gas measuring burette, the layer of magnesium is heated to redness, and the heat is then gradually extended to the lower part of the tube containing the mixture. The usual precautions are taken in adjusting the zero of the burette and in reading the volume of hydrogen. The method is useful for the examination of hydrocarbon oils.

Naphthenes may also be separated from paraffins by the sulphur dioxide method of Moore, Morell and Egloff (see page 9).

Destructive Distillation.—Non-volatile organic substances heated without access of free oxygen undergo complex decomposition, by which volatile products escape and a residue of impure carbon is left. If the substance consists only of carbon, hydrogen, and oxygen the last two elements are found in the distilled portions, together with a great part of the carbon. Sulphur and nitrogen are also principally converted into volatile compounds. Slow heating will sometimes produce volatilisation with little or no change. The nature and proportions of the substances obtained will be dependent on the character of the substance distilled, the temperature of the retort, and other conditions; when the heat is moderate, paraffins are chiefly produced; but as the higher members of this series readily split up into lower members and olefines, the latter are nearly always present. By further degradation acetylenes are formed, while benzene and its homologues contain a still smaller proportion of hydrogen.

When the temperature is high, hydrogen, acetylene, benzene, and naphthalene are the chief unoxygenated products. Thus, *coal* being distilled at a high temperature for the manufacture of coal-gas, the condensable hydrocarbons consist chiefly of benzene and its homologues, naphthalene, etc. At lower temperatures the products contain a larger proportion of paraffins and unsaturated hydrocarbons, with a correspondingly lower proportion of aromatic compounds. It has been shown that there is a maximum formation of benzene, toluene, and xylene at about 800°, 700° and 600° respectively (Whitaker and Crowell, *J. Ind. Eng. Chem.*, 1917, **9**, 261). Below about 600° little or no benzene is formed.

At a dull red heat, such as is employed for the distillation of bituminous shale, the liquid products are almost free from benzene and naphthalene, while little or no hydrogen or acetylene is present in the gases. On the other hand, the distillate is rich in paraffins and olefines with some anthracene and chrysene; the oxygenised and nitrogenised products consist chiefly of substances of the formula $C_nH_{2n-7}OH$, and other phenolic compounds, and bases of the formula $C_nH_{2n-5}N$ (pyridine bases), although the corresponding series, C_nH_{2n-6}—*i. e.*, benzene and its homologues—is almost wholly absent.

When *wood* is subjected to dry distillation, the volatile products are practically free from compounds of nitrogen and sulphur. The watery portion of the distillate from wood, peat, and lignite has an *acid* reaction, owing to the presence of acetic acid. In other respects the products of the distillation of wood, as ordinarily conducted, are a mixture of low- and high-temperature products.

When the temperature of the distillation is low, a large yield of liquid products is usually obtained, together with a small yield of gas of high illuminating power. At a high temperature a maximum production of gas of low illuminating power results, while the proportion of liquid products is small. The higher the temperature of the retort, the larger the percentage of solid carbonaceous residue (coke or charcoal) left in it.

The three cases afforded in practice by the treatment of coal, shale, and wood may be regarded as typical of the changes attending the destructive distillation of organic substances, though others, such as bone, rosin, and oil, yield special products of practical interest. It is probable that the course of reactions in the distillation of coal and the "cracking" of petroleum oils is similar; the kind and proportions of the products vary in a similar manner according to temperature at which the cracking is carried out. Paraffins of high molecular weight are decomposed at high temperatures into olefines, with decomposition products, naphthenes, etc., which in turn yield benzene and its homologues. Too much stress cannot be laid on the fact that the nature of the products depends not only on the nature of the substance treated, but also on the circumstances under which the operation is conducted with regard to temperature and other conditions.

The following table indicates the general nature of the more prominent volatile organic products of the dry distillation of coal (for the manufacture of illuminating gas), bituminous shale, and wood, *as the processes are carried on in practice.* To facilitate comparison, the leading constituents of American petroleum are shown in juxtaposition:

Organic products	Coal	Bituminous shale	Wood	Petroleum
Hydrogen	Large	Traces	Large	Present
Gaseous Hydrocarbons				
Methanes	Large	Large	Large	Present
Olefines	Large	Large	Considerable	Present
Acetylenes	Present	None	....	....
Liquid and Solid Hydrocarbons				
Liquid paraffins	Small	Large	Absent	Very large
Solid paraffins	Traces	Considerable	Present	Moderate
Liquid olefines	Small	Very large	....	Considerable
Liquid pseudolefines	....	....	....	Present
Liquid acetylenes	Present	Present	....	....
Benzenes	Large	Trace	Moderate	Present
Naphthalene	Large	None	Moderate	None
Anthracene	Moderate	Trace	....	Present
Chrysene	Moderate	Considerable	Present	Present
Oxygenated Bodies				
Acetic acid	Present	Present	Large	....
Methyl alcohol	None	....	Considerable	....
Phenols	Large	Considerable	Moderate	....
Hydroxyphenols (creosote)	....	Large	Large	....
Nitrogenised Bodies				
Ammonia	Considerable	Considerable	None[1]	....
Aniline bases	Present	None	....	....
Pyridine bases	Considerable	Considerable	....	....
Acridine	Present	....	....	....
Carbazole	Present	....	....	....
Sulphur Compounds	Present	Present	None	Present

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[1] Ammonia and other bases are sometimes present in small amounts and give rise to "blue" alcohol in copper rectification stills unless they are removed from the vapours by means of sulphuric acid. Amer. Ed.

It will be seen from this table that the products of the distillation of each of the raw materials contain certain characteristic bodies. Thus, oxygenated products are found most largely in the products of the distillation of wood; paraffins are *especially* characteristic of petroleum; olefines, and, to a less extent, paraffins, of the distillation of shale; while coal-tar, as obtained in the manufacturing of illuminating gas, is remarkable for the comparatively large proportion of benzene and naphthalene contained in it.

TARS

By the destructive distillation of organic substances and bituminous minerals three classes of products are generally obtained —namely, gas, watery liquid, and a viscid, dark-coloured oil or tar. The methods of analysing the gaseous products do not come within the scope of this work. The watery liquid from wood, peat, and lignite is acid, and its examination is described in Vol. I. The watery liquid from the distillation of coal, shale, and bones is strongly alkaline, the first of these constituting the "ammoniacal liquor" of the gas works.

TAR is a brown or black viscid, oily liquid, of a more or less characteristic odour, according to its origin; its composition varies widely according to its source and the conditions of distillation. Wood, peat, and lignite tars are acid; coal, bituminous shale, and bone tars are alkaline. On repeatedly agitating the tar with water, the soluble matters to which the acid or alkaline indication was due may be more or less completely removed.

All tars consist largely of hydrocarbons, but oxygenised and nitrogenised substances are sometimes present in considerable proportion. All tar, being of very complex composition, and consisting in the main of volatile bodies, the most instructive method of examining it consists in subjecting it to careful distillation, collecting apart the distillates obtained at different temperatures, and subsequently fractionating these products with the view of effecting a more perfect proximate analysis of the material. Toward the end of the distillation the tar remaining in the retort becomes more and more viscous, and, if allowed to cool, sets to a solid, brittle, jet-black mass known as *pitch*. If the distillation be pushed further, *coke* is obtained, and, indeed, in some cases distillation always causes coking.

Tar frequently contains a considerable proportion of water which should be separated as far as possible before distillation. This is best effected by allowing the tar to stand in a warm place, giving the mass an occasional gyratory motion, and removing each quantity of water by decantation as it separates. Water causes tar to froth during distillation; Mallmann ("Bitumen," 1909, 7, 117) states that a tar from which water readily separates on standing will be difficult to distil, and *vice versa.*

For the method of conducting the distillation, no general instructions can be given; much depends on the character of the tar, the information desired, the scale on which the operation is to be conducted, and other conditions. The process should be conducted in the simplest suitable apparatus, and the distillate collected in a very moderate number of fractions, all refinements of fractional distillation being reserved for the treatment of the products first obtained. In the first distillations the more volatile constituents are retained in the retort by those of higher b. p., and it is only after being separated tolerably perfectly from these that they distil at temperatures approximating to their true b. p.

The separation by fractional distillation having been carried out as far as appears desirable, a further proximate analysis of the different fractions may be made into basic, acid, and indifferent bodies. Thus, by agitating one of the fractions with dilute sulphuric acid, any basic compounds (*e. g.*, ammonia, methylamine, pyridine, acridine, etc.) will be dissolved in the acid liquid, and can be recovered by appropriate means. On agitating the residual oil with sodium hydroxide solution, first dilute, and then somewhat concentrated, any organic acids, phenols, or phenolic compounds will be dissolved, and can be recovered by separating the alkaline liquid and adding a slight excess of dilute sulphuric acid. The neutral substances which have not undergone solution either by the treatment with acid or with alkali consist essentially of hydrocarbons. Particular processes are suitable for special purposes. Thus, benzene may be crystallised out by subjecting the more volatile fraction of coal-tar naphtha to a freezing mixture; naphthalene readily separates from oils containing it, especially after removal of the phenols by sodium hydroxide; while the presence of anthracene can be inferred from the formation of anthraquinone by the oxidation of a certain high-boiling fraction of the tar. The hydrocarbons of the different series may be successfully differentiated in many cases by their behaviour with reagents, especially with bromine, nitric acid, and strong sulphuric acid.

The following sections contain detailed descriptions of the characters and methods of examining tar from bituminous shale and coal. Tars of some other origins are also briefly described.

SHALE TAR. CRUDE SHALE OIL

The crude oily liquid obtained in the south of Scotland by the destructive distillation of bituminous shale is an olive-green, strongly-smelling, viscous liquid. The sp. gr. of the product from the old form of retorts is 0.890 to 0.894, and from the new kind 0.865 to 0.870. The composition of shale oil has not been so thoroughly investigated as that of coal-tar, but it has been proved to be of extremely complex nature, the following being among the more characteristic and important substances hitherto recognised in it, unsaturated compounds predominate probably on account of the low hydrogen content of shale.

Hydrocarbons of the Methane series; most of the members from C_4H_{10} to $C_{30}H_{62}$ being probably present.

Hydrocarbons of the Olefine series; most of the members from C_4H_8 to $C_{20}H_{40}$ being probably present.

Hydrocarbons of the Allylene series; e. g., C_6H_{10}, C_7H_{12}, and C_8H_{14}.

Hydrocarbons of the Benzene series; present only in small amount, but always found in the oils from modern retorts.

Only traces of naphthalene and anthracene are found in shale tar, but notable quantities of pyrene and chrysene occur.

Nitrogenised compounds. Shale tar contains ammonia, a considerable proportion of pyrroline, and members of the pyridine series (especially those of high b. p. and unknown constitution), but neither aniline nor any of its homologues have been detected.

Oxygenated compounds. Besides traces of acids of the acetic series, shale tar contains a notable proportion of phenols and hydroxyphenols analogous to those present in wood-tar. Thymols and analogous bodies have been found in the fraction distilling between 215° and 290°.

Sulphur compounds exist in shale tar, but their exact nature has not been ascertained. Shales containing much sulphur give little paraffin wax on distillation, and a low yield of other products.

The method of treating shale tar on a large scale differs in different works, but consists essentially in repeated fractional distillations, alternated by treatment of the several fractions with sulphuric acid and sodium hydroxide, and sometimes sodium carbonate, together with refrigeration of the high-boiling fractions to cause the crystallisation of solid paraffin. This is separated from the adhering oil by pressure, and the crude paraffin scale which results is purified by appropriate methods.

American shale oils generally contain from 12% to 28% of saturated compounds and Scottish oils about 30% to 40%. An oil has been obtained from Nevada containing as much as 41% of saturated compounds. The saturated and unsaturated hydrocarbons of shale oil may be approximately estimated by vigorously shaking a sample of the oil with twice its volume of concentrated sulphuric acid then centrifuging the mixture; the saturated hydrocarbons are represented by the volume of the undissolved oil.

Large quantities of oil-bearing shale, known as Kukkerite, are obtained in Esthonia which on distillation yields about 70 gallons per ton of an oil of sp. gr. 0.92 to 0.93, from which a light oil of sp. gr. 0.79 may be separated and a heavy oil of higher density and b.p.; both factions consist mainly of unsaturated aliphatic hydrocarbons.

A laboratory method for the testing of oil shale for its yield of oil is given by Lomax and Remfrey (*J. Inst. Pet. Tech.*, 1921, 7, 34). A retort is made from a length of about 20 in. of 3-in. iron pipe which is reduced by sockets at either end. This is mounted horizontally and fitted for the introduction of steam at one end and connected at the other end in series with a condenser, cooled receiver for the oil, another condenser and wash bottles filled with oil to act as scrubbers, and an aspirator filled with water to measure the gas yield. One kilo. of the shale is placed in the retort and heated, then steam at 180° is passed into the retort, and the temperature gradually and uniformly raised throughout the mass until a dull red heat is reached. The volume of crude oil is measured, and its chemical and physical constants may be determined in the usual manner. Such tests should include the sp. gr., m.p., sulphur and water contents, and a fractional distillation with the separation of the following fractions; light naphtha below 150°, heavy naphtha 150° to 200°, light kerosene 200° to 250°, heavy kerosene 250° to 300°.

Ammonia can be estimated in the same apparatus by varying the method of heating. Broken firebrick is placed in both ends of the retort and shale in the middle; the ends are both heated to redness, then the shale in the middle is heated by steam and afterwards to a dull redness. The ammonia evolved is, after condensation, collected in dilute sulphuric acid and titrated as usual. By heating the shale in this way much gas and little oil is obtained.

Analysis of Crude Shale Oil.—The examination of crude shale oil is frequently required, in order to ascertain the proportions of naphtha, burning oil, lubricating oil, and "scale" or crude paraffin wax it is likely to yield on a large scale. The analysis is best made by treating a known quantity of the oil as nearly as possible in the same manner as that employed in the manufacturing process, but working on the small scale losses are, of course, very much larger; to diminish these as far as possible, all vessels, cloths, etc., are rinsed with oils similar to those to be handled, and the quantities of acid and alkali used are smaller than in the works. Each oil works has its own method of analysis, but the general features of the methods are similar, and all use measurements in preference to weights, and divide their fractions in a somewhat arbitrary manner. In a works laboratory the analyst knows fairly well what to expect from a particular sample, but when dealing with a strange oil it is best to make a preliminary test by distilling a portion without steam, collecting all below 150° as "spirit;" from 150° to 300° as "burning oil," and all above 300° (the thermometer having been withdrawn) as heavy oils. The following notes are due to the kindness of one of the best known of the Scottish oil chemists. In this process all measurements are calculated to 60° F.; the oils are usually measured at higher temperatures, and the necessary correction made (the sp. gr. is lowered 0.004 by each rise of 10° F. above 60° F.); the solid paraffin is weighed and its volume calculated, the sp. gr. in the liquid state at 60° F. being taken as 0.810.

1,300 c.c. (20,000 fluid grains) of crude oil freed from water by standing at 120° F. are distilled from a copper or cast-iron still, in a slow current of superheated steam; this distillation being destructive, excess of steam causes too much oil to pass over unchanged, and the subsequent treatments give misleading figures. 1,000 fluid grains of distillate are taken as "green naphtha," the remainder as "green oil," though some crude oils give, toward the end, so much "gundy" (chrysene, etc.) that this is kept separate; "still coke" remains in the retort. The green oil—in a stoppered bottle—is well shaken for 5 minutes with 0.25% of oil of vitriol (to remove moisture); then, at a temperature of 100 to 105° F., it receives 2% oil of vitriol, is shaken for a further 5 minutes and allowed to settle for 2 or 3 hours at 100° to 120° F. Next, the oil is washed with an excess of sodium hydroxide solution of 60° Tw.(1.300 sp. gr.), allowed to settle in a warm place, the alkali tar removed, and the oil again distilled with superheated steam—40% being collected as "light oil" and the remainder as "heavy oil and paraffin." The heavy oil is cooled slowly (to obtain large crystals), first to the room temperature, then in a freezing mixture, wrapped in a cloth previously wrung out with "blue oil" and pressed at 60° F., giving solid paraffin ("hard scale") and "blue oil." The blue oil, after treatment with 0.5% of oil of vitriol and with sodium hydroxide, is distilled with 1% of dry sodium hydroxide, yielding light oil and lubricating oil; the 2 light oils—from the "green oil" and the "blue oil"—are mixed, treated with 0.25% oil of vitriol and sodium hydroxide, and again distilled, yielding burning oil and intermediate oil; the intermediate oil, treated like the heavy oil, gives a further yield of solid paraffin ("soft scale").

The methods of examining the naphtha, burning oil, lubricating oil, and paraffin scale which form the proximate products of the distillation of crude shale oil are described in the section on "Petroleum and Shale Oil Products."

Blast-furnace Tar

Blast-furnace tar has some of the characters of a low-temperature tar, but differs materially in composition from ordinary gas retort tar. It contains only a very small proportion of low phenols but large quantities of the higher cresols. Watson Smith (*J. Soc. Chem. Ind.*, 1883, **2**, 495 and 1887, **6**, 583) gives the following figures for tar produced by blast furnaces consuming bituminous coal. The sample had a sp. gr. of 0.954, and on distillation gave the following results:

	Percentage of products	Sp. gr.
Distillate below 230°	Water, 30.6 by volume Oil, 2.9 by volume	1.007 .889
Distillate from 230° to 300°	7.0 by volume	.971
Distillate from 300° till oils solidify	13.0 by volume	.994
Distillate solidifying on cooling, or soft paraffin scale	16.7 by volume	.987
Coke	21.5 by weight	....
Loss	5.5 by weight	....

On further fractionation and treatment with sulphuric acid and sodium hydroxide the following products were obtained:

	Per cent. by volume
Tar bases, soluble in sulphuric acid	10.6
Phenols and tar-acids, soluble in sodium hydroxide	5.6
Neutral oils	18.2
Soft paraffin scale	5.7

(Yielding solid paraffin 0.54%)

The phenolic compounds are further described under the head of "Blast Furnace Creosote."

Of the neutral oils, only an insignificant fraction distilled below 180°. The sp. gr. of successive fractions rose from 0.858 to 0.980. No naphthalene could be separated from an appropriate fraction by cooling it with ice and salt. The intermediate oils were not specially good as lubricants, nor were they suitable for burning in lamps. The fractions distilling between 250° and 350° possessed a deep green fluorescence, and closely resembled heavy lubricating oil from shale. On treating the soft paraffin scale with glacial acetic and chromic acids, solid paraffin was obtained, and a large proportion of a pitchy deposit was formed, but no anthraquinone, produced by the oxidation of anthracene, could be detected.

Wood-tar.—The products of the destructive distillation of wood are very numerous, and vary much with the nature of the wood and the temperature at which the process is conducted. But under all circumstances the volatile products are characterised by the large proportion of oxygenised products contained in them, and by the small proportion of sulphur and nitrogen compounds. Among the gaseous products are carbon dioxide, carbon monoxide, hydrogen, and some methane. The aqueous portion of the liquid distillate, known as *crude pyroligneous acid*, usually forms from 28 to 50% of the weight of wood distilled, and contains chiefly acetic acid, methyl alcohol allyl alcohol, and acetone, with many other substances in smaller proportion.

Distillation of two samples of wood-tar showed the following proportions, which are characteristic:

Water	52.8%	32.3%
Oil to 250° C.	12.6%	15.8%
Pitch	30.6%	51.9%

Tar is also separated by distillation of the crude pyroligenous acid; this usually contains a very much larger proportion of pitch and little tar-oil. On distillation between 70° and 250°, Russian wood-tar yields oils of a density ranging from 0.841 to 0.877, and leaves a residue of *pitch*, consisting of solid paraffin, various resinous matters, pyrene, chrysene, and other hydrocarbons of high b. p.

On redistillation the tar-oils yield the following products:

Below 100°; fatty acids, sylvane (C_5H_6O), methyl alcohol, benzene.
Between 100° and 150°; benzene homologues.
Between 150° and 200°; benzene homologues, phenols, and hydroxyphenols.
Between 200° and 250°; phenols and hydroxyphenols, lignoceric acid ($C_{24}H_{48}O_2$), naphthalene, retene, paraffin wax.

The lower paraffins appear to be absent from the tar, but the permanent gases produced by the distillation of the wood contain methane. If the oils of wood tar are exposed to a high temperature, they are partially converted into heavy gaseous hydrocarbons. "Wood-gas is manufactured in this manner, and contains, when purified:

Hydrogen	48.7 to 18.7
Methane	35.3 to 9.4
Ethylene and its homologues	10.6 to 6.5
Carbon monoxide	61.8 to 22.3

80% of the more volatile portion of Swedish wood-tar consists of a mixture of two terpenes: australene, boiling at 155°; and sylvestrene, boiling at about 175°. The most important product from wood-tar is the mixture of phenolic compounds known as creosote, the method of examining and the nature of which are described later.

Stockholm tar, used in ship-building, is the product of a crude distillation of the resinous wood of the pine. It contains much resin and turpentine, and has applications for which the tar obtained in the manufacture of pyroligneous acid cannot be substituted. It has a sp. gr. of 1.04, and on standing usually deposits a granular, crystalline matter consisting mainly of *pyrocatechol*. Water agitated with the tar acquires a light brown colour and a sharp, bitterish taste. The aqueous liquid is coloured transiently green by ferric chloride, owing to the pyrocatechol; lime water acquires a permanent brownish-red colour. When Stockholm tar is heated, water, acetic acid, and impure turpentine oil are volatilised and ordinary *pitch* remains.

COAL-TAR

Coal-tar being a product of destructive distillation, its composition varies with the details of the distillation, and there are marked differences between tars obtained in the manufacture of coal-gas, and those collected at the coke ovens; when coal-tar is mentioned without any qualification, that from the gas works is usually referred to.

Gas-works Tar.—This is a black viscid fluid, with a strong and characteristic odour; its sp. gr. ranges from 1.08 to 1.25.

The composition of this tar depends much upon whether a horizontal retort of the old fashioned type or a more modern vertical retort has been employed. In the vertical retort the escaping vapours pass through the coal at lower temperatures with the result that less breakdown of hydrocarbons occurs and probably some solvent action is exerted on the coal itself in the upper layers. The effect of the introduction of vertical retorts is to lower the sp. gr. of the tar which contains less pitch and more tar-oils. Horizontal-retort tar may contain 60% to 70% of pitch with 30% to 40% of oils; vertical-retort tar contains about 40% to 45% of pitch with 55% to 60% of tar oils, the amount of benzol and naphthalene present is quite small and although the total tar-acids extractable with sodium hydroxide is larger than in horizontal-retort tar the amount of real phenol is quite small. The following table (see W. A. Walmsley, *J. Soc. Chem. Ind.*, 1922, **41**, 296) shows the different composition of the two classes of tars:

	Vertical tar, sp. gr. 1.091		Horizontal tar, sp. gr. 1.175	
	Sp. gr.	Yield	Sp. gr.	Yield
Ammonia water	1.025	4%	1.003	3.0%
Crude naphtha	0.946	2.59%	0.925	1.34%
Light oil	....	....	1.007	6.02%
Middle oil	0.996	30.91%	1.025	6.18%
Creosote	1.053	20.09%	1.045	16.32%
Pitch	....	41.47%	....	66.56%
		99.06		99.42
Viscosity (Redwood at 100° F.)	....	345 sec.	....	610 sec.
Free carbon	....	1.19%	....	11.5 %
Calorific value (B.Th.U.)	....	16,120	....	16,150
Pitch volatile matter	....	69.9 %	....	53.0 %
Fixed carbon	....	30.0 %	....	47.0 %
Free carbon	....	5.0 %	....	25.0 %
Ash	....	0.1 %	....	0.1 %

Tar from vertical retorts contains about half the quantity of naphthalene present in that from horizontal retorts.

The first treatment of coal-tar on a large scale consists in distilling it and collecting the distillate in three or four fractions. The temperatures at which the receivers are changed differ considerably in the practice of different works, and hence the products are far from being identical. The following table represents three methods of fractionation which are largely employed:

A		B		C	
Product	Distilling point, °	Product	Distilling point, °	Product	Distilling point, °
Crude naphtha or light oils	0 to 170	First runnings, or first light oils	0 to 110	Light naphtha	0 to 110
Heavy oils, dead oils, or creosote oils	170 to 270	Second light oils	110 to 210	Light oil	110 to 170
		Carbolic oils	210 to 240	Carbolic oils	170 to 225
		Creosote oils	240 to 270	Creosote oils	225 to 270
Anthracene oils	above 270	Anthracene oils	above 270	Anthracene oils	270 to 360
Pitch	....	Pitch	....	Pitch	....

The arrangement on page 44, taken with certain alterations from a table published by E. J. Mills, shows the general method of treating coal-tar in works employing method C of original fractionation.

During the first part of the process permanent gases are given off, while the fluid distillate consists of ammoniacal water and the most volatile constituents of the tar proper, together with sensible traces of less volatile compounds, carried over mechanically or volatilised in company with the steam, etc. The ammoniacal liquor forms a lower layer which can be readily separated from the first light oils. The point when the shoot should be changed is indicated pretty accurately by a "break" or comparative cessation of distillation, together with a peculiar noise known as "the rattles." On further heating the distillation recommences, and the second light oils come over regularly. The point for again changing the shoot is, in some works, that at which a sample of the distillate sinks in water, whilst in other cases the solidification of the distillate on cooling, from the crystallisation of naphthalene, is the indication relied on. At a higher temperature a distillate is again obtained, which remains liquid on cooling. The commencement of the anthracene oil period may be ascertained by a thermometer immersed in the *vapour*, but is commonly deduced from the quantity of the distillate. It may also be considered to commence at the point at which the distillate again deposits solid matter on being completely cooled. Sometimes the anthracene oils are subdivided into first and second "green oils" and "red oil." The distillation is sometimes stopped when the oil sets to the consistence of butter on cooling, but may be pushed as far as possible short of actual coking, the residue remaining in the retort consisting of hard pitch, which, after cooling, is run out into tanks. Owing to the fall in the value of anthracene, however, the anthracene oil fraction is now rarely worked. The distillation is stopped at the end of the creosote oil period, and the anthracene left in the pitch, which then requires no addition of softening oil.

The proportions of the various products obtained necessarily vary largely with the character of the tar distilled and the details of the mode in which the operation is conducted. These differ in different works and in the same works at different times.

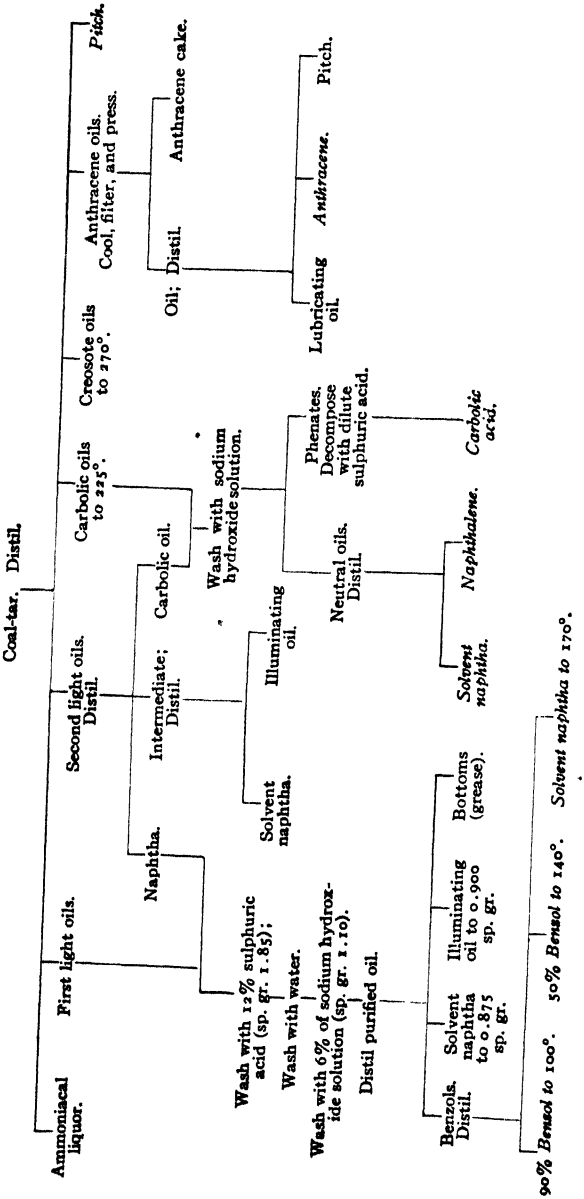
If the coal is distilled at a low temperature, a considerable amount of paraffins and other open-chain compounds are formed; distillation at high temperature increases the proportion of closed-chain hydrocarbons. At high temperature, however, much carbon is deposited in the free state by contact of the distilling substances with the hot walls of the retort. The resulting gas is, therefore, lighter than that produced at a low temperature. This fact is practically applied in filling large balloons. When possible, the engineer works a bench of retorts at a high temperature, and thus obtains a gaseous mixture containing more methane and free hydrogen, and hence of greater lifting power, than a gas from a lower heat. For yields of English tars, see page 47.

The general composition of the various fractions obtained by the distillation of coal-tar will be regulated chiefly by the b. p. of the leading constituents, but the vapour-densities, vapour-tensions, and relative abundance of the constituents of the tar also largely affect their behaviour in the still. Thus, naphthalene is always found in notable quantity in all the fractions from second light oils to anthracene oil, and is even deposited from the purified illuminating gas itself. Owing to the high temperatures generally employed in the gas works at the present time, the quantity of naphthalene in all the fractions coming from the tar is very greatly increased, so that with most tars the light oil as well as the creosote fraction will completely solidify on cooling to the ordinary temperature.

Constituents of Coal-tar.—(For a full discussion of the constituents and products of coal-tar see M. Meyer, *Zeit. angew. Chem.*, 1909, **22**, 338 and 391.) The following summary of the more important constituents of gas-works tar is compiled from Lunge's "*Coal-tar and Ammonia*," fifth edition.

I. *Hydrocarbons.*
  - (*a*) Paraffins, CH_4 to $C_{27}H_{56}$.
  - (*b*) Olefines, C_2H_4 to C_7H_{14}.
  - (*c*) Naphthenes, C_6H_{12} to C_8H_{16}.
  - (*d*) Acetylenes, C_2H_2 to $C_{16}H_{28}$.
  - (*e*) Naphthylenes, C_6H_{10} to C_8H_{14}.
  - (*f*) Terpenes, C_6H_8 to $C_{10}H_{16}$.
  - (*g*) Benzenes, C_6H_6 to $C_{10}H_{14}$.
  - (*h*) Naphthalenes, $C_{10}H_8$ to $C_{12}H_{12}$.
  - (*i*) Anthracene and phenanthrene, and their homologues.
  - (*k*) Pyrene, chrysene, picene, etc.

II. *Oxygen Compounds.*
  - (*a*) Water.
  - (*b*) Alcohols (?).
  - (*c*) Acetone.


Coal-tar. Distil.
Ammoniacal liquor.
First light oils.
Second light oils. Distil.
Carbolic oils to 225°.
Creosote oils to 270°.
Anthracene oils. Cool, filter, and press.
Pitch.
Naphtha.
Intermediate; Distil.
Carbolic oil.
Wash with sodium hydroxide solution.
Oil; Distil.
Anthracene cake.
Wash with 12% sulphuric acid (sp. gr. 1.85);
Wash with water.
Wash with 6% of sodium hydroxide solution (sp. gr. 1.10).
Distil purified oil.
Solvent naphtha.
Illuminating oil.
Neutral oils. Distil.
Phenates. Decompose with dilute sulphuric acid.
Lubricating oil.
Anthracene.
Pitch.
Benzols. Distil.
Solvent naphtha to 0.875 sp. gr.
Illuminating oil to 0.900 sp. gr.
Bottoms (grease).
Solvent naphtha.
Naphthalene.
Carbolic acid.
90% *Benzol to 100°.*
50% *Benzol to 140°.*
Solvent naphtha to 170°.

- (*d*) Acetic and benzoic acids.
- (*e*) Phenol and cresols.
- (*f*) Naphthols.
- (*g*) Coumarones.

III. *Sulphur Compounds.*

- (*a*) Hydrogen sulphide.
- (*b*) Ammonium sulphide and thiocyanate.
- (*c*) Sulphur dioxide.
- (*d*) Carbon disulphide.
- (*e*) Thiophenes and thiotolenes, etc.
- (*f*) Mercaptans.

IV. *Nitrogen Compounds.*

- (*a*) Ammonia and its salts.
- (*b*) Alkylamines.
- (*c*) Anilines.
- (*d*) Pyridines, C_5H_5N to $C_{12}H_{19}N$ (?).
- (*e*) Quinolines, C_9H_7N to $C_{11}H_{11}N$.
- (*f*) Acridines.
- (*g*) Pyrrole.
- (*h*) Cyanides and methyl isocyanide.
- (*i*) Carbazoles, $C_{12}H_9N$, etc.

Analysis of Coal-tar.—The analysis of coal-tar is sometimes limited to a laboratory operation in which the various fractions are collected as nearly as possible under the same conditions as those which obtain on the large scale, though the details will necessarily vary with circumstances. With practice, good results are obtained with as small a quantity as 300 grm. of the tar, the yields corresponding closely with those given on a large scale. The following mode of operation is that recommended by B. Nickels: 250 c.c. of the tar is placed in a retort which it only one-third fills, so as not to spoil the distillate if there is much frothing during distillation. The retort should be supported on a cup-shaped piece of coarse wire gauze, placed in an aperture in a sheet-iron plate. Over the retort is placed a dome, made by removing the bottom from a tin can or bottle and cutting out a piece of the side to allow the neck of the retort to pass through. This contrivance confines the heat, and prevents the distillate or heavy vapour from falling back; indeed, without some such arrangement a satisfactory analysis of coal-tar in glass is nearly impossible. The products obtained by the distillation are: (1) ammoniacal liquor; (2) total light oils; (3) creosote oil; (4) anthracene oils; and (5) pitch. In obtaining these fractions, the character of the distillate is amply sufficient to indicate the point at which the receiver should be changed. No thermometer is necessary, nor need any condensing arrangement be attached to the retort. A powerful bunsen should be used, as toward the close of the operation it is necessary to maintain the wire-gauze at a red heat. The ammoniacal liquor and naphtha are collected together in a graduated cylinder, which is changed as soon as a drop of the distillate sinks when collected in a test-tube of water. After standing, to allow perfect separation of the *ammoniacal liquor* and *light oils*, the volume of each is observed, and, if desired, the strength of the former can be ascertained in the usual way by distillation with lime and titration of the distillate. The quantity of light oils is too small for further fractionation.

The next fraction of the distillate consists of *creosote oil*. At first it will contain much naphthalene, and will probably solidify in white crystals on cooling, but afterwards a more fluid distillate is obtained. At a still later stage a drop of the distillate collected on a cold steel spatula will be found to deposit amorphous solid matter of a yellow or greenish-yellow colour; the receiver is now again changed, the fraction measured, and, if desired, analysed for phenol and naphthalene, as described in the section on "Creosote Oils." With many tars this fraction is semi-solid, and must be measured while quite warm.

The next fraction of the distillate is rich in anthracene, and not infrequently condenses in the neck of the retort as a yellow, waxy substance, which may be melted out by the local application of a small bunsen flame.

The collection of *anthracene oil* is complete when no more distillate can be obtained, and the pitch intumesces and gives off heavy yellow fumes. The distilled fraction is then measured and cooled thoroughly, and the resultant pasty mass pressed between folds of blotting-paper, weighed, and analysed for real anthracene by the anthraquinone test. The result is calculated into *crude anthracene* at 30%, a standard which is generally adopted by manufacturers.

When the distillation for anthracene oil is complete, the retort may be allowed to cool, and when almost cold its body should be plunged into cold water. This produces a rapid surface-cooling and shrinking of the pitch from the glass; the latter may then be broken and removed by gentle tapping, leaving the cake of *pitch* clean and ready for weighing.

The following figures, communicated by B. Nickels, show the results obtained by the examination of four representative samples of London tar. The apparent excess is due to the tar having been measured and the pitch weighed:

	A	B	C	D
Ammoniacal water	2.5	3.7	8.0	5.0
Total light oils	2.5	3.4	0.5	3.2
Carbolic and creosote-oils	21.3	17.0	23.0	20.0
Anthracene oils	17.0	17.0	13.0	13.0
Pitch (grm. per 100 c.c.)	59.4	60.0	58.0	62.0
	102.7	101.1	102.5	103.2
Pressed anthracene	4.0	......	1.15	......
Containing real anthracene	13.4%	......	25.68%	
=30% crude anthracene in tar	1.8	1.47	1.3	1.12

The following are typical analyses of tars from London gas works using Durham coal.

	A	B
Ammoniacal liquor	3.9	3.1
Naphtha	1.63	1.56
Carbolic oil	11.87	12.00
Creosote oil	4.37	4.3
Anthracene oil	21.87	22.21
Pitch	53.65	54.44
Loss on distillation	2.71	2.39
	100.00	100.00

The reviser is indebted to Mr. Ernest F. Hooper for the foregoing figures, as also for the following analysis of tar obtained by distilling Ruhr coal in a Dessau vertical retort:

Water	1.5
Light oils	3.6 to 338° F.
Medium oils	15.5 to 446° F.
Heavy oils	11.6 to 518° F.
Anthracene oil	30.0 to 716° F.
Pitch	37.0

Mr. C. C. Tutweiler, of Philadelphia, has furnished the following copies of routine analyses of coal-tar, made from two typical American coals.

Sp. gr., 1.227 Water, 13.2% by vol.
Free carbon, 23.68% by wt. } Dry tar
Dry tar Distillation test

Crude products of distillation	Per cent. by volume	Per cent. by weight	Sp. gr.	Description of fractions
Light oils (below 338° F.)				
Middle oils (338°-518° F.)	17.8	14.41	0.993	Yellow oil and naphthalene
Anthracene oils (above 518° F.)	37.3	33.40	1.099	Med. red
Residuum		49.50		Hard, black, and porous
Total	55.1	97.31		

Sp. gr., 1.232 Water, ——% by vol.
Free carbon, 27.43% by wt. } Dry tar
Dry tar Distillation test

Crude products of distillation	Per cent. by volume	Per cent. by weight	Sp. gr.	Description of fractions
Light oils (below 338° F.)	0.56	0.37	0.824	Light green
Middle oils (338°-518° F.)	15.68	13.55	1.064	Red. green
Anthracene oils (above 518° F.)	29.23	26.34	1.110	Dark red brown
Residuum		55.91		Black and brittle
Total	45.47	96.17		

While the foregoing method of analysis is useful for works purposes, more exactly defined methods are necessary for comparing different samples of tar, or for forming an opinion as to their suitability for particular purposes. A critical review of standard methods of analysis used in the coal-tar industry is given by (Weiss, *J. Ind. Eng. Chem.*, 1918, **10**, 732, 817, 911, 1006).

1. **Specific Gravity.**—This should be determined at 15.5°, and as most tars are too viscous at this temperature for the use of an ordinary hydrometer or a pykrometer, the method given on page 59 or page 182 should be employed.

2. **Water.**—This is always estimated by distillation. When the water content only is to be estimated a known volume of the tar may be diluted with approximately its own volume of toluene or naphtha and the mixture distilled up to 170° in a metal flask. The volume of water is then measured in the distillate. For this purpose a copper still 6 in. by 3½ in. with a clamped on lid and a ring burner is most convenient. 50 c.c. of naphtha are measured into a cylinder, 200 c.c. of the tar added and the bulk poured into the still and washed in with a further 150 c.c. of naphtha. Heat is applied by means of a ring burner and the distillation continued up to 205° (170° is sufficient to expel all water from the still, but the higher temperature insures flushing out the condenser tube). The distillate is collected in separating funnel previously moistened with benzene; this effects a clean separation of the water and allows its volume to be accurately read after a few minutes standing. When, however, it is intended to proceed with the distillation test the water may conveniently be estimated at the same time. For the **Distillation Test** a weighed quantity of about 500 grm. of the tar is introduced in a glass distillation flask of about 1 litre capacity connected to a Liebig condenser, and placed on a wire gauze or a sand bath. The thermometer bulb should be level with the lower edge of the side tube and the range of the thermometer be not less than 80° to 330°. When the distillation temperature reaches 200° it is best to allow the water to run out of the condenser and use it as an air condenser. The fractions should be collected as under:

(*a*) Water (ammonical liquor)	up to 170°
Light oils	
Middle oils	170° to 270°
Heavy oils	270° to 300°
Pitch	above 300°

The American Society for Testing Materials recommends a somewhat different procedure (*cf.* Weiss, *loc. cit.*) 100 c.c. of the tar is subjected to distillation in a 250 c.c. distillation flask of specified dimensions and fractions are collected thus:

Start of distillation to 110°; 110° to 170°; 170° to 235°; 235° to 270°; 270° to 300°; and residue.

3. **Free Carbon.**—Some controversy has ranged round the question of the most suitable solvent for this test, as it has been suggested that insoluble compounds are formed by some solvents result-

ing in a high value for the free carbon. The most approved solvent is 90% benzol. Five grm. of the tar are weighed into a Soxhlet extraction thimble and extracted by boiling the benzol under a reflux condenser until the benzol runs through clear.

The ordinary Soxhlet extractor is quite suitable for this purpose, but the top of the thimble should be at a higher level than the top of the siphon tube. The apparatus shown in the figure, originally proposed by Church, has the merit of simplicity and is useful for this estimation.

4. **Viscosity or Consistence.**—This may be determined in the usual way by means of Redwood's or Engler's Viscometer, but for viscous tar the float test described by the U. S. Office of Public Roads (Weiss, *loc. cit.*) or Hutchinson's Viscometer (below) are useful, although their readings cannot be translated into absolute units.

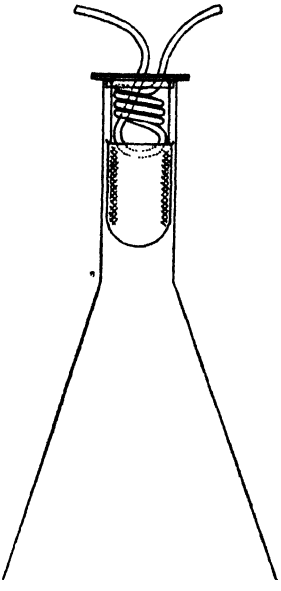


Fig. 3.—Estimation of free carbon in tar.

The Ministry of Transport (Roads Department) of Great Britain has drawn up specifications[1] for tars used for road making purposes;

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[1] General Directions and Specifications Relating to Tar Treatment of Roads. H. M. Stationary Office, London, 1923.

tar No. 1 is for spraying and No. 2 for making tar macadam. It is specified that the tars should not contain more than 15% of water-gas tar. The specifications are as under:

Requirements to be fulfilled on testing	Specification 3(*a*) Tar No. 1	3(*b*) Tar No. 2
Sp. gr. at 15°, not more than	1.225	1.240
Water or ammoniacal liquor not more than	1.0% by weight	1.0% by weight
Other distillate (light oils) below 170°, not more than	1.0% by weight	
Distillate between 170° and 270° middle oils, within the range.	12.0% to 24.0% by weight	10% to 18% by weight
Distillate between 270° and 300° heavy oils, within the range.	4.0% to 12.0% by weight	6.0% to 12.0% by weight
Phenols or crude tar-acids, not more than	5.0% by volume	4.0% by volume
Naphthalene, not more than	8.0% by weight	5.0% by weight
"Free carbon" not more than	22.0% by weight	24.0% by weight
Consistence or viscosity, at 25°, within the range	3.0 to 20.0 seconds	20.0 to 100.0 seconds

The methods of analysis adopted by the Department for the estimation of phenols and naphthalene, and for measurement of viscosity are as follows. Phenols or crude tar-acids are estimated by bringing the distillate of middle oils to a temperature of 40° to 50°, adding to them about 20% of solution of sodium hydroxide having sp. gr. 1.20, and shaking vigorously every 5 minutes while keeping the mixture at 40° to 50°. At the end of 15 minutes the mixture is poured into a tap-funnel, and, after the solution of sodium hydroxide has settled out, this solution is run off into a measuring cylinder. The extraction is repeated with a similar amount of fresh sodium hydroxide solution which is separated and mixed with the first extract. The contents of the cylinder are then made slightly acid by the gradual addition of hydrochloric acid. The volume of tar-acids which are liberated is read off, and the percentage calculated on the volume of tar taken for the distillation.

To estimate the naphthalene, the distillate of middle oils, after separation of the phenols, is weighed, warmed sufficiently to dissolve all the naphthalene in it, well agitated, and an aliquot part of not less than 25 grm. taken. This part is cooled to 15° and kept at that temperature for half an hour. The naphthalene which has separated out is then filtered off with the aid of a pump, pressed between folds of filter paper until all the oil has been removed by the paper; the naphthalene is then weighed, and the percentage calculated on the weight of tar taken for the distillation.

The consistence or viscosity is to be ascertained, not by Engler's or Redwood's apparatus, as is frequently done, but by means of a special hydrometer—Hutchinson's tar tester or viscosity gauge No. 2 poise being used. This instrument (see Fig. 4), which is 9 in. in length and is supplied with three poises for use with tars of different viscosities, is used thus. The tar is placed in a cylindrical vessel of at least 9 in. depth and of 3¾ to 4 in. internal diameter, filling it to within ½ in. of the top; the tar is brought to a uniform temperature of 25°, then the gauge with the No. 2 poise is allowed to sink into the tar, and the time in seconds occupied in sinking by that portion of the stem between the rings *A* and *B* indicates the consistency of the tar.

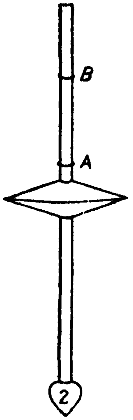

Fig. 4.—Hutchinson tar tester.

The increasing use of tar for road purposes has led, in some cases, to the contamination of streams by drainage from roads containing tar acids, which are disastrous to fish life, and it is necessary to distinguish between pollution arising from tar and that from vegetable matter. Fox and Guage's method for the estimation of tar-acids in road drainage (*J. Soc. Chem. Ind.* 1920, **39**, 260 T., 1922, **41**, 173 T.) requires the following solutions. (1) Sulphanilic acid 1.91 grm. in 250 c.c. of water. (2) Pure sodium nitrite 0.85 grm. in 250 c.c. of water. (3) Sulphuric acid 1 part to 3 parts of water. (4) 8% sodium hydroxide solution. (5) Standard solution containing mixed cresols 1 grm. per litre (the mixture of cresols consists of 35: 40:25 of *o*- *m*- and *p*-cresols).

Diazotised sulphanilic acid solution is prepared about 5 minutes before use by mixing 5 volumes of sulphanilic acid solution with 1 volume of the sulphuric acid, adding 5 volumes of sodium nitrite solution and cooling in a stream of cold water. The cresol solution used for comparing the colour is a dilute solution prepared by diluting 5 c.c. of the cresol solution (5) with 95 c.c. of water. (*i. e.* 1 c.c. of the dilute solution = 0.00005 grm. of cresol), and should be freshly prepared just before use.

To make the test 100 c.c., (or less of a strong tar extract) of the clear water or washings are placed in a Nessler cylinder, and 5 c.c. of the sodium hydroxide solution added, followed by 10 c.c. of the diazotised sulphanilic acid. On stirring, an orange coloured dye is formed when tar acids are present. The depth of colour is matched by adding to a similar quantity of distilled water in another cylinder 2 c.c. of the dilute standard cresol solution, 5 c.c. of the sodium hydroxide solution and 10 c.c. of the diazotised sulphanilic acid. This is a trial assay and determines the amount of the cresol solution to be used to obtain an exact matching of the depth of colour due to the tar acids in the water under test. As it is not always possible to match exactly the shade of dye by the above solution of cresols, xylenol or naphthol standards may be used if necessary. These are prepared by making up solutions containing 0.00005 grm., per c.c. from the fraction of the acids from coal tar boiling between 205° and 230°, and from β-naphthol respectively. According to the colour to be matched the standard solution should contain cresols, tar acids or naphthol, or a mixture of the three, but the total weight of the phenolic substances per c.c. should be the same in all cases. The same authors give (*loc. cit.*) a method for the estimation of tar bases in drainage waters.

COKE-OVEN TAR

The rapid spread of patent coke ovens with recovery of by-products has, of course, resulted in the production of very large quantities of coke-oven tars, and these tars show marked differences from gas-works tar. The ovens may be regarded as of two types—first, such as the beehive (from which tar is rarely obtained) and the Jameson, where air is admitted to the oven; and, second, those (Simon-Carvé, Otto-Hilgenstock, and many others) in which the oven is externally heated by gas and the access of air prevented as far as possible. Those of the first class yield tars very similar to those obtained from blast furnaces or by distillation of shale; they are usually lighter than water, contain little or no benzene, naphthalene, and anthracene, but considerable quantities of paraffins. The externally heated ovens, on the other hand, yield tars somewhat similar to those obtained from the gas works, and are examined and utilised in the same way. The temperatures in these retorts are high and the distillation lasting 24 to 30 hours, cracking takes place; consequently these tars are poor in light oils, but rich in both naphthalene and anthracene.

The following is a typical analysis of a tar obtained by distilling a Durham coking coal in Otto-Hilgenstock ovens:

The sp. gr. of the tar was 1.198 and it contained 10.5% of free carbon. 1,000 grm. distilled from a copper still gave the following fractions:

Ammoniacal liquor	2.4	
Light oil (to 170°)	1.4	
Carbolic oil (170°–230°)	8.0	(filtered and pressed gave 3.6 oil and 4.4 crude naphthalene.)
Creosote oil (230°–270°)	9.8	(of which 3.3 = oil, 6.5 crude naphthalene.)
Anthracene oil (270° and upward)	24.8	(17.8 anthracene oil; 7.0 crude anthracene.)
Pitch	51 8	
Loss	1.8	

Examining the tars from various coke ovens using Durham coking coals, and taking 50 gallons of tar for each experiment, Mr. Ernest F. Hooper obtained the following figures (private communication):

	Simon-Carvé	Otto	Otto-Hilgenstock
Water	4.5	4.0	4.0
Naphtha	0.5	0.6	0.25
Light oils	1.0	1.5	1.75
Creosote oil	17.4	15.7	18.0
Heavy oil	18.6	13.7	10.0
Pitch	58.0	63.0	66.0
	100.0	98.5	100.0

WATER-GAS TAR

In many illuminating gas plants, particularly in the United States, a large portion of the gas is made from carburetted water gas—water gas, into which, while incandescent, a stream of petroleum oil is injected. The tar from this form of gas-making is quite useful. Benzene, toluene etc., naphthalene, creosote oil and pitch or coke are obtained. When first produced it contains about 50% of water, the separation of which offers some difficulty, but is now effected by a centrifugal process at a moderate temperature. It differs in composition from ordinary coal-tar in containing very little paraffins, bases, phenols, or free carbon.

German water-gas tars have sp. gr. only a little above that of water, and contain about 25% of water. After removal of the water they have a composition approximately as under:

Light oils up to 230°	22%
Heavy oils up to 300°	30%
Heavy oils up to 330°	13%
Pitch	30%
	95

In great Britain much tar is made from Mond producer gas, such a tar had the composition:

Water	16.8%
Light oils up to 170°	3.9%
Oils 170°–230°	2.0%
Oils 230° to pitch	22.9%
Pitch	54.4%

The following works analyses of American water-gas tars are furnished by Mr. C. C. Tutweiler.

Sp. gr.,	1.092
Free carbon,	trace

Crude products of distillation	% by volume	% by weight	Sp. gr.	Description of fractions
Light oils (below 338° F.)	1.39	1.09	0.8557	Colourless
Middle oils (338°–518° F.)	16.84	14.87	0.9585	Greenish-yellow
Anthracene oils (above 518° F.)	59.23	57.28	1.056	Deep red
Residuum		24.72		Black and brittle
Total	77.46	97.96		

Sp. gr.,	1.083	Water, 4.25% by vol.
Free carbon,	0.73%	

Crude products of distillation	% by volume	% by weight	Sp. gr.	Description of fractions
Light oils (below 338° F.)	3.97	3.68	0.9255	Yellow
Middle oils (338°–518° F.)	28.44	28.27	0.9939	Yellow
Anthracene oils (above 518° F.)	36.62	39.66	1.0831	Dark red green fluorescence
Residuum		24.10		Hard, black, porous
Total	69.03	95.61		

PEAT TAR

Tar obtained by distillation of peat is stated by E. and F. Bornstein (*J. Gas. Lighting*, 1915, **129**, 731) to have the following composition:

Water	48.5%
Light oils 150° to 170°	1.8%
Middle oils 170°–230°	4.7%
Middle oils 230°–270°	10.7%
Heavy oils 270°–330°	24.7%
Coke	9.4%

This tar yielded 18% of phenols, 1% of tar-bases, 34% of oils and 47% of pitch, extraction showed it to contain 24% of paraffin wax of m. p. 65°. The oils obtained from distillation of peat-tar differ from the oils of coal tar in being highly unsaturated, so much so that they absorb oxygen from the air.

TAR-OILS

The uses of the intermediate fractions from coal-tar distillation have of late years been much extended and include the preparation of lubricating oils, transformer oils, fuel oils, and oil for froth-flotation processes. The tar acids, phenols, etc. are usually removed by washing with alkali hydroxide, and the product is a heavy tar-oil having sp. gr. usually above 1.01.

The estimation of phenol[1] and naphthalene will be given in respective sections. Almost all tar-oils suitable for use in Diesel engines: their calorific power is generally above 16,000 B.t.u. per lb. and their lower hydrogen content as compared with mineral oils makes the difference between gross and net values less than for petroleum products. The ignition point is high, usually about 480°. The most important point in connection with these oils as fuel is the ash content, which should not exceed 0.05%. The ash is usually soft, being composed largely of sodium sulphate arising from the washing process.

The German specification for tar-oils for this purpose requires that:

1. The oil shall not contain more than 0.1 grm. of residue insoluble in xylene when 25 grm. are shaken with 25 c.c. of xylene and the insoluble matter filtered off through a tared paper and washed with hot xylol.
2. The water must not exceed 1.0%.
3. The coke must not exceed 3.0%.

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[1] For a more accurate method of estimating phenol in tar or tar-oil see Weiss and Downs (*J. Ind. Eng. Chem.*, 1917, **9**, 509); or Fox and Barker (*J. Soc. Chem. Ind*, 1918, **37**, 265, T.); and Petrie (*J. Soc. Chem. Ind.*, 1919, **38**, 132, T.).

4. At least 60% by volume should distill below 300°.
5. The calorific power must not be less than 8800 calories per grm.
6. The open flash point must not be lower than 56°.
7. The oil must be quite fluid at 15°.

The following table shows the average results of the analysis of tar-oils as used or fuel purposes. (Moore, Tar-oils for Diesel Engines).

	Maximum	Minimum	Average
Sp. gr.	1.090	0.950	1.017
Water, per cent	12.0	0.00	1.08
Sulphur, per cent	1.02	0.28	0.64
Ash	0.10	0.00	0.005
Closed flash point	208	97	164
Viscosity Redwood units at 70° F	6.8	23	8.6
B.T.U. (gross)	17,946	16,400	17,360
B.T.U. (net)	17,174	15,903	16,597
Coke yield, per cent	14.7	1.3	3.3
Free carbon, per cent	5.2	0.00	0.26
Tar acids, per cent	30.0	trace	9.5

Valenta has shown that the benzene hydrocarbons which constitute coal-tar oils are completely soluble in dimethyl sulphate at ordinary temperatures, whereas petroleum products, rosin oils, etc., are not soluble. A method based upon this observation is therefore available for the differentiation of coal-tar oils from mineral oils. Since all mineral oils are not insoluble in this solvent the method is not quantitative (see Harrison and Perkin, *Analyst*, 1908, 33, 2). Dimethyl sulphate is shaken with half its volume of the oil to be tested, the bulk of the aromatic oil and some of the mineral oil being thereby dissolved; the solution is then saponified with alcoholic potassium hydroxide solution; the hydrocarbon oil, mixed with only a little mineral oil, is thus recovered and may be identified as an aromatic oil.

Another reagent which has been proposed for this purpose and which may be used for the quantitative estimation of tar-oils in admixture with mineral oils is wet aniline, (Holde and Weill, *Brennstoff Chem.*, 1923, 4, 177). The mixture is shaken with wet aniline, this dissolves out the coal-tar oils, leaving the mineral oil with a little aniline in solution. On washing the aniline solution of tar-oils and the mineral oil solution of aniline with dilute hydrochloric acid complete separation may be effected. Rosin oils also are somewhat soluble in wet aniline.

Tar-oil, in the proportion of about 1 lb. per ton, is used for froth-flotation; its value depends upon its power of wetting the coal or mineral to be separated; hence is dependent upon the surface tension of the oil, which should be low between the oil and coal and coal or mineral, and high between oil and water. Wood tar-oils are found particularly useful for this purpose.

COAL-TAR PITCH

This is the residue remaining in the still after the first distillation of coal-tar, and usually amounts to about ⅔ of the weight of tar operated on. Its physical characters depend somewhat on the kind of coal distilled and the point at which the distillation was arrested. Thus, soft pitch is obtained if the process is stopped when the oils distilling have a sp. gr. of about 1.090, and hard pitch if it is continued until the sp. gr. of the products distilling reaches 1.120. In order to obtain a large yield of anthracene, the distillation is sometimes pushed as far as possible, and the residual hard pitch diluted with a certain proportion of creosote oil or anthracene oil, whereby a product of any requisite softness can be obtained. A compounded pitch of this sort will yield a notable quantity of liquid oils when distilled, and, possibly, naphthalene, which last is much objected to.

The proximate composition of pitch is little understood. It always contains small quantities of the higher boiling tar oils, such as naphthalene, anthracene, chrysene, etc., but the bulk of it consists of fusible carbon compounds, of still higher b. p. (termed collectively "tar bitumen") and, in addition, so-called "free carbon" is also present. This latter remains behind on successive extraction of the pitch with benzene, carbon disulphide, and alcohol, as an infusible black powder, resembling anthracite, but by no means consisting of elementary carbon. Thus, Behrens obtained from a pitch 23.54% of such a powder, containing 8.19% of hydrogen, and 0.4–0.9% of ash. The amount of this "free carbon" increases with the carbonisation temperature, so that the amount found in tar and pitch is now much higher than formerly, as much as 30% being sometimes found in tar, and over 40% in pitch.

Soft pitch can be easily kneaded between the teeth, but moderately hard pitch with difficulty only, whilst hard pitch crushes to powder. Soft pitch is blacker and more lustrous than hard pitch, which often has a grayish tint and is somewhat porous. In the latter case it is partly coked, and is unfit for making patent fuel, for which pitch of but moderate hardness is preferred. The sp. gr. of hard pitch ranges from 1.275 to 1.300, and that of a soft pitch from 1.240 to 1.270.

Soft pitch	softens at 40° and melts at about 60°.
Moderately hard	softens at 60° and melts at about 80°.
Hard	softens at 80° and melts at about 120°.

Contract notes for pitch intended for exportation to the Continent often stipulate that a sample is to "twist fairly after immersion for two minutes in water at 60°, but not under 55°; must contain at least 53% of volatile organic matter; and must be free from any extraneous matter, such as sand or grit."

The following analyses made by S. S. Sadtler show some of the differences between water-gas pitch and coal-tar pitch.

	Water-gas pitch	Standard coal-tar pitch
Sp. gr.	1.21	1.29
Softening-point	107.3° F.	106.8° F.
M. p.	147.2° F.	141.8° F.
Loss by evaporation at 329° F. during 7 hours	5.25%	2.51%
Percentage of free carbon	5.43%	28.80%
Distillate above 572° F.	25%	29%
Green oil fraction	(liquid)	(semi-solid)
Extracted with petroleum spirit	10.74%	7.55%

PITCH TESTS

Pitch testing is still in an unsatisfactory condition, so much depending upon the personal factor and upon the precise conditions under which any particular test is carried out.

Specific Gravity.—The sp. gr. of pitch may be determined by means of Westphal's balance or by any of the methods commonly used for the sp. gr. of solids. A rapid and convenient method is to dilute a solution of calcium chloride of sp. gr. 1.40 with water until a lump of the pitch, free from air bubbles, just begins to sink in the liquid. The sp. gr. of the solution is then taken by means of a hydrometer as usual.

Melting Point.—On rise of temperature pitch gradually changes from a brittle slow-flowing material to a viscous liquid; there is no definite temperature at which it can be said to melt. Consequently the so-called m. p. is an arbitrary temperature depending upon prescribed conditions. Methods most commonly used are those of F. G. Holmes and of Spielmann and Petrie (*J. Soc. Chem. Ind.*, 1919, **38**, 68, T.). Holmes' method is as follows:

A ½ in. cube of the pitch is fastened upon a piece of copper wire, No. 16 gauge, by heating the wire sufficiently to force it through the cube; after this is done, the wire is bent close to the cube into a right angle and suspended in the beaker containing 500 c.c. of water so that the bottom of the cube is exactly 1 in. from the bottom of the beaker.

The water in the beaker should have a temperature of about 15°, and in case of pitch of low m. p. or soft pitch, 5 minutes should be allowed before applying the heat. It is of advantage to use water which has been previously boiled to expel dissolved air and cooled. This minimises the collection of bubbles on the cube.

The temperature of the water is taken by a thermometer suspended in the beaker with the bottom of the bulb on a level with the bottom of the cube of pitch.

The temperature is raised 5° each minute and the temperature when the pitch just touches the bottom of the beaker is considered the m. p.

Softening-point or Twisting-point.—If the softening-point is also to be ascertained, a larger beaker with 500 c.c. of water is used, and several cubes of pitch are hung in the water. The temperature is raised at the same rate of speed, *i. e.*, 5° per minute. Cubes are removed and twisted from time to time, and when the cube can be twisted around 2 or 3 times without breaking, the softening-point is reached. The test may be continued until the m. p. is reached.

In case the pitch melts above 90° or 95° (194°–203° F.), it will be necessary to use a solution of calcium chloride in water, or brine, in which to take the m. p. Glycerin may also be used. It is necessary that the pitch should have either a heavier or lighter sp. gr. than the solution used. In cases where the sp. gr. is lighter the pitch will rise in the solution, and the temperature at which it just reaches to the surface is taken as the m. p.

Weiss (*J. Ind. Eng. Chem.*, 1918, **10,** 817) recommends the foregoing method for pitches having m. p. not higher than 77°. Above this temperature a specially arranged air oven is employed. Spielmann and Petrie's method gives concordant results usually about 18° or 20° lower than those by the Holmes method. A pitch block 1½ × ½ × ½ in. is prepared either by cutting the sample with a hot knife or by melting it and running it into a mould. This is fixed on to a piece of No. 17 gauge copper wire bent into an "L" shape with a foot ¾ in. long by plunging the hot wire into side of the block at a point ½ in. from one end. The block is cooled for 3 hours and then suspended 2 in. below the surface of freshly boiled cold water in a 750 c.c. beaker. The bulb of a thermometer is placed level with the block, and the water stirred and its temperature raised 1° per minute until the upper horizontal edge of the block comes in line with the upright copper wire. Stirring is continued till the temperature begins to fall and the maximum temperature observed is taken as the softening-point of the sample.

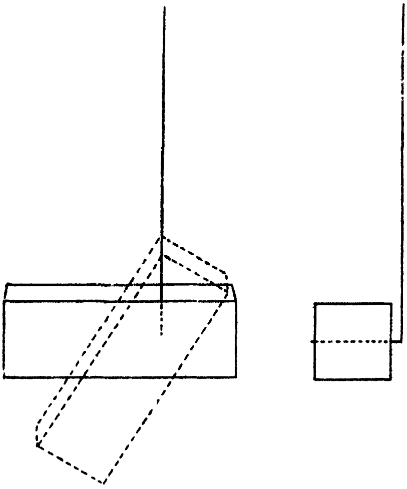

FIG. 5 Spielmann and Petrie's method.

Breaking-point.—A ½ in. cube of pitch is fastened to a copper plate by melting slightly so that it adheres firmly. It is then placed in tepid water and allowed to remain 5 minutes. The point of a knife blade is now slid along the plate till it touches the pitch, and then forcibly and slowly raised through the pitch. If the pitch is still soft, it will push its way through, but if the breaking-point is reached the pitch will scale off with a conchoidal fracture. The temperature of the water is slowly lowered by the addition of water and allowing the pitch to stand for 5 minutes between trials.

The Slide Test.—A ½ in. moulded cube of pitch is placed on a grooved copper plate inclined at an angle of 30° and kept in an oven at the temperature of exactly 40° (104° F.) for 12 hours. The length of the stream of pitch is measured in inches, and is used for comparison of different pitches to be used for a given purpose. The grooved plate has several grooves so that several samples may be tested at the same time.

The Evaporation Test.—10 grm. of the pitch are heated in an air-bath for 7 hours at exactly 160° (320° F.) and the percentage loss noted.

Free Carbon Estimation.—1 to 5 grm. of pitch are accurately weighed in a weighed extraction thimble, Schleichler and Schull, 80 × 22 mm., and first extracted with hot toluene (about 90°). Suspend the thimble in a beaker, so that it does not touch the bottom or sides, by passing a fine wire through the top of the thimble and pour in successive portions of toluene, but not into the thimble. After soaking for two hours in the toluene, the thimble is transferred to a Soxhlet extractor and suspended by the wire so that it does not touch the bottom and extracted with hot benzene, occasionally changing the solvent benzene, and continuing until the solvent becomes colourless, finally drying the thimble and weighing.

Volatile Matter.—The proportion of volatile organic matter in pitch ranges from 47 to 64%. It is estimated by gradually heating 1 grm. (in some works, 5 grm.) of the carefully sampled and powdered pitch in a platinum crucible until distillation ceases. The operation should occupy about fifteen minutes, and must not be hurried, or the pitch may swell up and even boil over the sides of the crucible, leaving a very porous residue. A cover with a small aperture in the centre is then placed on the crucible, which is placed in a crucible-jacket and further heated for ten minutes over a powerful bunsen, and finally for ten minutes over a blast-flame. The residual *coke*, which should be dense and graphitoidal, is then weighed, and the volatile organic matter calculated from the loss. With care and attention to details the test gives constant results, but otherwise very discordant figures may be obtained. The coke may be burned and the proportion of ash ascertained if the presence of *sand* or *grit* is suspected.

The **Penetration test** is used more in America than in England. The New York testing laboratory penetrometer or the Dow penetrometer are the more usual forms and are instruments in which a weighed needle is arranged to press upon the sample kept at a specified temperature; the distance the needle has penetrated in, say, 5 seconds with a given load expresses the penetration (*cf.* Weiss *loc. cit.*).

Oil Pitch.—Oil pitches are used to a large extent in America for architectural, road-making, and insulating purposes; they exist in many varieties depending on the kind of oil from which they may have been produced and differ materially in composition, melting point and hardness.

Mineral oil pitch is valuable on account of its toughness and flexibility at low temperatures and resistance to acids and alkalies; it finds use in varnish making, for which coal tar pitch is unsuitable. Pitch from vegetable oils also finds use in varnish making and for insulating purposes.

Mansbridge (*J. Soc. Chem. Ind.*, 1918, **37**, 182, T.) gives the following figures for different varieties of American mineral oil pitch:

Sp. gr. at 15.5°	1.023 to 1.060
Flash point open °F	390 to 572
Flash point closed °F	360 to 495
Fire test °F	460 to 610
Solubility in	
(*a*) Petroleum spirit (0.680)	61% to 75%
(*b*) Carbon tetrachloride	99.9% 99.8
(*c*) Carbon disulphide	99.8%
Ash	0.1% to 0.2%
Melting point, cube °F	112° to 300°
Paraffin wax	0.3% to 0.7%
Sulphur	3.7% to 5.6%
Penetration test at 77° F	175 to 20

The following scheme for the identification of pitches is given by the same author (*loc. cit.*) but does not apply to mixtures except in a general way. The scheme is based on the separation of pitches into two classes by their behaviour with alcoholic solution of potassium hydroxide; these classes are subdivided by treatment with "white spirit" of b. p. 140° and sp. gr. 0.75 to 0.80.

The sample is boiled with alcoholic solution of sodium or potassium hydroxide in a porcelain basin until nearly dry:

Section 1. The sample is wholly or partly saponified. Stearine pitch, all varieties, woolgrease pitch or bone pitch.

Section 2. No saponification takes place. Coal tar group. Mineral oil group. Natural asphaltum. Ozokerite pitch. Wood tar pitch.

Section 1. Boil about 0.6 grm. in 10 c.c. of white spirit, allow the mixture to settle for a few minutes, decant or filter and examine the residue. The substance dissolves:

(*a*) Stearine pitch from all non-drying fats.

(*b*) Wool grease pitch. This may be recognised by its tenacity when melted and by the presence of cholesterol.

The substance partly dissolves:

(*a*) Pitch from semi-drying or drying oils and fats, including soft cottonseed pitch; this is usually oxidised when testing m. p. The insoluble portion is in broken films or scales which powder when rubbed between the fingers.

(*b*) Bone pitch which gives a characteristic odour of bones when heated.

The substance is insoluble or nearly so:

(*a*) Hard cottonseed pitch (melts in a flame).

(*b*) Elastic cottonseed pitch, sometimes called rubber pitch. Does not melt in a flame, will stretch and return.

Section 2. Treat with white spirit as in section 1. The sample dissolves:

(*a*) Soft mineral oil pitch, of treacle-like consistence or very plastic.

(*b*) Natural asphaltums when free from mineral matter (ash). Hard and brittle with brilliant fracture.

The sample is only partly soluble:

(*a*) Nearly all mineral oil pitch. This is more or less plastic and has a very low ash, usually below 0.3%.

(*b*) Natural asphaltum when containing mineral matter. Hard brittle and can be powdered; ash high and often visible with a lens in the sample.

(*c*) Ozokerite pitch. Fracture rough, waxy when heated, will burnish with a warm bright iron.

(*d*) Trinidad pitch, plastic to brittle according to m. p.; hard varieties very dull rough fracture, with high ash, not visible.

The sample is insoluble: the spirit is coloured yellow and becomes highly fluorescent.

(*a*) Coal tar group, including blast furnace and coke oven pitch. These give a characteristic smell when heated.

(*b*) A few mineral oil pitches which give an asphaltum smell when heated.

(*c*) Wood tar pitch, giving a woody smell when heated, like Stockholm tar.

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BITUMENS

BY SAMUEL P. SADTLER, Ph. D. L. L. D.

A class of substances consisting of hydrocarbons and products derived from them by alteration, occurs associated together in nature, and is collectively known as "bituminous." They may be gaseous, liquid, or solid and very frequently all three of these physical modifications are found admixed in the same crude material. As, on the other hand, they occur at least outwardly in separate form, they will be separately noted.

NATURAL GAS

Broadly speaking, we should include here, because of analogy of composition, not only the gas from gas wells, which have developed in the boring for petroleum or for salt, but the "fire damp" accumulating in coal mines and the "marsh gas" obtained from stagnant pools or springs containing decomposing vegetable material. However, we will confine ourselves to the industrial product known as natural gas as it occurs in association with the production of petroleum. This natural gas accumulates in the upper part of the oil and gas-bearing deposits, being trapped in sand stone formations of loose texture, in shale seams and in cavities. It may or may not be in immediate association with liquid petroleum. It is known as "wet" or "dry" according to this association. Dry gas consists chiefly of methane with some ethane and propane. The wet gas on the other hand contains in addition some higher members of the same series like butane, pentane and hexane, volatile hydrocarbon liquids which may be withdrawn from the mixture by the methods of compression or adsorption and then yield very valuable light gasoline. The compression method has been in the past the one mainly used, but it is probable that in the future the adsorption method will be more largely adopted. Activated charcoal is now used for the adsorption of gasoline from natural gas at ordinary temperature. This will adsorb all the gasoline from a current of the gas passing at the right velocity and take up 22 to 25% of its weight in gasoline. This is then distilled from the charcoal by means of superheated steam.

The composition of a number of typical samples of natural gas is shown in the accompanying table of analyses taken in part from Bacon and Hamor (*American Petroleum Industry*) and in part from Brooks (*Chemistry of the Non-benzenoid Hydrocarbons*).

TYPICAL ANALYSES OF NATURAL GAS

	Methane, %	Other hydrocarbons, %	Carbon dioxide, %	Nitrogen, %	Other constituents, %
West Los Angeles, California	91.00	2.70	1.00	5.20	0.10
Santa Maria, Santa Barbara Co., Cal	62.70	20.20	15.50	1.40	0.20
Fredonia, Chautauqua Co., New York	90.05	....	0.41	9.54	....
Kane, McKean Co., Pa	90.38	....	0.21	9.41	....
Murraysville, Westmoreland Co., Pa	97.70	....	0.28	2.02	....
Fairmount, Marion Co., W. Va	81.60	14.29	0.10	3.21	0.80
Iola, Allen Co., Kansas	94.50	....	....	5.08	Helium, 0.18
Elmdale, Chase Co., Kansas	78.60	8.26	0.15	12.13	Helium, 0.56
Dexter, Kansas	14.85	0.41	....	82.70	Helium, 1.84
Eureka, Kansas	51.40	....	....	46.40	Helium, 1.50
Fort Worth, Texas	51.30	10.40	0.10	38.20	Helium, 0.90
Boro Island, Can	87.60	0.90	....	11.20	Helium, 0.33

The presence of large percentages of nitrogen in several cases is no doubt due to admixture with atmospheric air, the oxygen of which has been consumed in the oxidation of sulphides. This source of the nitrogen may also explain the presence of the helium in these gases.

Natural gas finds its largest utilization as fuel for both industrial and domestic purposes. A considerable amount is also used in the production of "Carbon Black," used in the manufacture of printer's ink, black varnishes and typewriter ribbons.

The Fortworth Texas gas quoted in the table as containing 0.9% helium is being treated by the U. S. Government in its plant at Petrolia, Texas, for the extraction of helium for use in the Government dirigible balloons.

The analysis of natural gas is universally carried out by the means of absorption pipettes, which have been so improved as to give quite accurate results. The Orsat-Burrell apparatus used for this analysis is described by G. A. Burrell and G. G. Oberfell (*J. Ind. Eng. Chem.*, 1916, **8**, 229). It is designed for the analysis of a gas mixture containing carbon dioxide unsaturated hydrocarbons, principally ethylene, oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen.

In the analysis the capillary train and U tube are swept free of gases by drawing a sample of air into the burette and passing it into the alkaline pyrogallate pipette *G* to remove oxygen. The residual nitrogen is then passed into all the pipettes and through the CuO tube to sweep out other gases that may have been contained therein. The electric current is now turned on the electric heating oven, the temperature having been established by previous experiments. About a 100 watt furnace is required. The temperature desired is between 275 and 300°. Some of the gas mixture is drawn into the burette, measured and passed into the pipettes *E*, *F* and *G* for the removal respectively of carbon dioxide, illuminants, and oxygen. After these constituents have been removed the stop cocks *H*, *I* and *J* are turned so that communication is made between the burette and the pipette corresponding to *J* and through the CuO tube. The gas mixture is passed back and forth through the tube furnace until no further diminution in volume is noted by reading the gas volume in the burette. Fifteen minutes is usually required, the carbon monoxide being converted to carbon dioxide and the hydrogen to water. The carbon monoxide burns more rapidly if any hydrogen is present. When the gas is cooled and no further contraction takes place the remaining volume is read in the burette. The carbon dioxide is now removed by passing the gas mixture into the KOH pipette *E*. After the hydrogen and carbon monoxide have been estimated the residual gas is placed in the KOH pipette for storage and the stop cock is closed. Enough oxygen to burn the paraffin hydrocarbons is then drawn into the burette, measured and passed into the slow combustion pipette *J* and the platinum spiral is heated to almost white heat. The residual gas is now withdrawn from the pipette *E* into the burette and from these slowly passed at the rate of not more than 10 c.c. per minute into the pipette *J*. While operating, it is well to cover the slow combustion pipette with gauze as occasionally, if the gas is passed in too rapidly, an explosion takes place. After combustion is complete, the contraction and the carbon dioxide are measured and the gas again passed in the slow combustion pipette and burned again. A small amount of further contraction may take place, but may be ignored unless excessive.

For calculation of results, the following example and formulæ are useful:

(In the analysis of natural gas, the estimations of hydrogen and carbon monoxide practically fall away from the considerations.)

ANALYSIS OF GAS FROM PRESSURE STILLS

(*a*) Volume of sample taken	44.1 c.c.	
(*b*) Volume after KOH absorption	44.0 c.c.	
(*c*) *Carbon Dioxide*—CO_2	0.1 c.c.	= 0.22%
(*d*) Volume after Br_2 or oleum absorption	39.4 c.c.	
(*e*) *Olefines or illuminants*	4.6 c.c.	= 10.43%
(*f*) Volume after alkaline pyrogallate absorption	39.3 c.c.	
(*g*) *Oxygen*, O_2	0.1 c.c.	= 0.22%
(*h*) Volume after burning in CuO	35.2 c.c.	
(*i*) *Hydrogen*, H_2	4.1 c.c.	= 9.30%
(*j*) Volume after absorption in KOH	35.0 c.c.	
(*k*) *Carbon Monoxide* CO	0.2 c.c.	= 0.45%
(*l*) Volume taken for slow combustion	17.5 c.c.	
(*m*) Oxygen added	75.6 c.c.	
(*n*) Total volume	93.1 c.c.	
(*o*) Volume after burning	61.5 c.c.	
(*p*) Contraction from burning	32.6 c.c.	
(*q*) Volume after KOH absorption	45.0 c.c.	
(*r*) Contraction from CO_2	16.5 c.c.	
(*s*) *Methane* in sample	16.0 c.c.	= 72.56%
(*t*) *Ethane* in sample	0.3 c.c.	= 1.36%
(*u*) *Nitrogen* in sample	1.2 c.c.	= 5.46%

Petroleum.—Rock Oil. Mineral Oil.

French—Pétrole. *German*—Erdöl. *Spanish*—Petrólea.

Petroleum is a natural oily liquid occurring in the earth at very varied depths, and in a great many localities. It is not confined to any particular geological formation. Thus, the petroleum of the great Pennsylvania field is derived from the Devonian and Carboniferous limestone formations, whilst that of California and Russia is found in Tertiary rocks. Petroleum may not be indigenous to the strata in which it is found; in some instances it has undergone distillation or been forced from one stratum to another by the pressure of gas and water. An exact definition of the use of the term Petroleum can hardly be given. The more viscous varieties may be nearly black in colour and contain such amounts of oxygenated constituents and sulphur (both free and combined) that make it partly asphaltic in its nature and hard to distinguish from a maltha (liquid asphalt). Commercial usage alone will draw the line between a heavy black petroleum and thin black maltha.

Petroleum has now been found or its presence definitely indicated in almost every country in the world. Following the United States production, which in 1921 was 472,439,000 barrels, comes that of Mexico, which in the same year amounted to 191,418,000 barrels, and then that of Russia and the Dutch East Indies. Very extensive deposits are indicated in Persia and Mesopotamia, and from the former source the Anglo-Persian Oil Co. has begun production of commercial products at the Llandarcy Refinery in South Wales, where the crude is brought in tank steamers from the Persian Gulf. Similar large but undeveloped deposits are known to exist in Venezuela and Colombia and the plant of Trinidad in the West Indies is producing, in addition to solid asphalt, about 3,000,000 barrels annually of an asphaltic petroleum. At present the American production so overshadows all others from a commercial point of view that the following description applies chiefly to that product:

Crude natural petroleum is an oily liquid, varying in density from 0.73 to 0.97, the Pennsylvania product ranging between 0.79 and 0.83. It has a characteristic odour, sometimes, but by no means invariably, disagreeable; its colour varies from straw-yellow to brownish-black. Its coefficient of expansion varies considerably with its sp. gr., as is shown by the following table:

SP. GR. AT 15°	EXPANSION-COEFFICIENT FOR 1°
Under 0.700	0.00090
0.700 to 0.750	0.00085
0.750 to 0.800	0.00080
0.800 to 0.815	0.00070
over 0.815	0 00065

On a stock of 1,000,000 barrels of petroleum, the shrinkage in winter amounts to 7,000 to 10,000 barrels as compared with the volume in summer.

Petroleum is insoluble in water, and but slightly soluble in alcohol, but it is miscible in all proportions with chloroform, ether, carbon disulphide, and hydrocarbons. It mixes readily with ordinary fixed oils, castor oil being an exception (Vol. 2, page 223). All varieties are combustible, burning with luminous, more or less smoky, flames.

Chemical Composition of Petroleum.—Chemically, crude petroleum consists of a mixture of a considerable number of hydrocarbons with small quantities of sulphur and sulphuretted, nitrogenised, and oxygenised substances.

According to Brooks (*loc. cit.* p. 29) ordinarily the proportion of nitrogen in petroleum does not exceed 1.5%, but an Algerian oil is reported as having 2.17% and a Japanese 2.25%. The highest percentage of nitrogen thus far reported is 2.39% found in a Californian oil. This means that probably 20% of that oil consists of nitrogen bases. Very little is known as to the character of these bases. They form precipitates from acid solutions with platinum, palladium, mercuric, cadmium and ferric chlorides, potassium dichromate, ferro- and ferricyanides and picric and oxalic acids. By oxidation with alkaline permanganate in alkaline solution the nitrogen is evolved partly as free nitrogen and partly as ammonia. These substances are weakly basic. In 1900 Mabery concluded that the nitrogen bases in California petroleum consisted of a mixture of more or less hydrogenated quinolines. Later (in 1920) he obtained evidence of the presence of a methyl-quinoline and other alkylated quinolines or isoquinolines.

According to Kast and Lagai (*Ding. Poly. Jour.*, 1892, **284**, 69), all crude petroleums, except that from Tegernsee, contain sulphur in amounts varying from 0.136 to 1.87% and as much as 7.5% has been found in Mexican oil. Mabery and Smith have investigated the nature of the sulphur compounds in California oils and find that they are in the form of alkyl sulphides; thiophen and mercaptans are absent.

Mabery and Quayle (*J. Soc. Chem. Ind.*, 1900, **19**, 505) investigated crude Canadian oils and isolated a series of alkyl sulphur compounds by distilling at a pressure of 50 mm., and at a later date (1906) they obtained evidence of the existence of hydrothiophanes which they designated as "thiophanes."

Richardson and Wallace (*J. Soc. Chem. Ind.* 1901, **20**, 690) have found free sulphur to be the form in which a large part, if not nearly all, of the sulphur in Texas (Beaumont oil) exists. Some hydrogen sulphide is dissolved in the oil and a large amount is formed if the oil is heated as in distillation, when it comes off in considerable quantities due to action of the sulphur upon some of the hydrocarbons.

Petroleum is variable in composition, and more or less volatile and mobile according to its content of bitumen and solid substances. In general, it contains about 85% of carbon and 15% of hydrogen, but its elementary composition gives no idea of the variety of hydrocarbons contained in it. In brief, the constituents of petroleum present the following varieties of character:

(*a*) Their volatility is very different, for they extend from gases of very low b. p. to solids which boil at high temperatures (370° and 450°).

(*b*) The volatility of the constituents is usually inversely as their sp. gr., the lightest oils being the most volatile.

(*c*) The inflammability is a function of the volatility, the more volatile constituents taking fire on approach of a flame at ordinary temperatures, while the denser and less volatile oils require to be heated considerably before they can be inflamed or made to give off inflammable vapors.

The hydrocarbons of petroleum belong to several series, the paraffins largely predominating in American petroleum, while members of other series are present in relatively large amount in the petroleum of other regions.

Pennsylvania petroleum has been most completely studied. A complete series of paraffins, from CH_4 to $C_{16}H_{34}$, has been obtained from it; and the solid members, $C_{25}H_{52}$, $C_{27}H_{56}$, and $C_{30}H_{62}$, are also present, especially in the oils from the Bradford (Penna.) district. Iso-paraffins, as well as the normal forms, exist in American petroleum. The paraffins from CH_4 to C_4H_{10} are gaseous at ordinary temperatures, and hence escape in admixture with hydrogen from petroleum wells, or when the petroleum is stored or gently heated. The members from C_5H_{12} to $C_{15}H_{32}$ constitute the greater part of the liquid portion of American petroleum, one of the most characteristic constituents being hexane. Mabery (*Proc. Am. Acad. Arts and Sciences*, **32**, 121, and **37**, 565) has isolated the hydrocarbons of Pennsylvania petroleum as well as most of the other oils from important localities. It is now generally believed that olefine hydrocarbons rarely, if ever, exist naturally in crude oil, but commonly result from its exposure to high temperatures. They are separated from aromatic compounds, paraffins and naphthenes by the action of concentrated sulphuric acid in the usual process of refining the oil. Naphthenes (polymethylenes), similar to those characteristic of Russian petroleum, are also present. Benzene and its homologues exist in traces in American petroleum.

The paraffin wax, removed by chilling, consists of heavy hydrocarbons of the C_nH_{2n+2} series but the lubricating oil derived from

Pennsylvania and other petroleums consists chiefly of hydrocarbons of the C_nH_{2n-2} series, but their structure is unknown and no pure individual hydrocarbons have been isolated from them. Vaseline isolated from Pennsylvania petroleum is a mixture of hydrocarbons of the empirical formulæ C_nH_{2n-2} and C_nH_{2n-4}.

Canadian petroleum contains various hydrocarbons of the paraffin and olefine series, and is richer in aromatic compounds and poorer in gaseous paraffins than the Pennsylvania product. Mabery (*Proc. Am. Acad. Arts and Sciences*, 1897, **32**, 156, and 1904, **40**, 334) has shown that the low b. p. hydrocarbons belong to the paraffin series and those above 196° to the olefine series. It contains a notable quantity of sulphur compounds and traces of benzene and nitrogenous basic oils. It yields about 3% of solid paraffin.

Californian petroleum contains, as shown by Mabery (*Proc. Am. Acad. Arts and Sciences*, 1901, **36**, 256, naphthenes, or polymethylenes and aromatic hydrocarbons. Sulphur compounds, with a notable amount of the esters of nitrogenous basic oils, have been shown to be present by Peckham and others.

Ohio petroleum is intermediate in properties between Caucasian and Pennsylvania oils, and contains the following: Methane, two butanes, pentane, isopentane, hexanes, heptanes, octane, nonane. These form less than 10% of the oil. The crude oil contains a large amount of sulphur compounds. Aromatic hydrocarbons are present in very small amount. The sulphur compounds have a tendency to collect in the higher fractions. Mabery has also carefully studied these oils (*Proc. Am. Acad. Arts and Sciences*, 1904, **40**, 323.

Petroleum from certain American fields contains no paraffins; for example, Coates (*J. Am. Chem. Soc.*, 1906, **28**, 384) has shown that the lighter distillates of the oil from Pennings, Louisiana field consist exclusively of cyclic series C_nH_{2n}.

Mexican oil is, in general, a heavy oil, largely composed of polymethylene hydrocarbons containing sulphur in notable amount and termed "asphalt-base" oil.

Russian petroleum is chiefly obtained in the neighborhood of Baku on the Caspian Sea, but is also found in other parts of the Caucasus. A fraction of given b. p. has a higher density than a similar fraction of American petroleum or Scotch shale oil, and the viscosity is more readily decreased by heat. It usually yields no solid paraffin.

This petroleum is scientifically interesting from its peculiar composition. Beilstein and Kurbatow could not obtain any products of constant b. p., even after nine distillations, nor were they able to extract any benzenoid hydrocarbons by treatment with fuming nitric acid, nor any olefines with bromine. Their researches, as extended by Schützenberger and Ionine, and by Markownikoff and Oglobini, have shown that Caucasian petroleum consists chiefly of a mixture of naphthenes, having the general formula C_nH_{2n}. These are isomeric with the ethylenes, and with the benzene hexahydrides (so-called paraffins, $C_nH_{2n-6}H_6$), obtained synthetically by Wreden. With the exception of the hydrocarbon $C_{13}H_{26}$, all the naphthenes from C_8H_{16} to $C_{15}H_{30}$ have been separated from Caucasian petroleum. They boil at somewhat lower temperatures than the isomeric olefines and the normal paraffins containing the same number of carbon atoms, and at approximately the same temperature, as the synthetically prepared paraffins; but the sp. gr. of the Caucasian hydrocarbons are notably greater than those of the isologous paraffins from most American petroleums. Thus, while normal octane, C_8H_{18}, boils at 124° and has a sp. gr. of 0.7188 at 0°, octonaphthene, C_8H_{16}, boils at 119° and has a sp. gr. of 0.7714. Similarly, $C_{12}H_{26}$ boils at 202° and has a sp. gr. of 0.7655, while $C_{12}H_{24}$ boils at 196° and has a sp. gr. of 0.8027 at 17°.

The naphthenes do not form nitro-derivatives, and resemble the paraffins in not yielding additive compounds and in being convertible into chlorinated derivatives from which alcohols are obtainable. When oxidised, the naphthenes form oxidation-products, or are converted into higher isologues.

The higher boiling portions of Caucasian petroleum probably contain hydrocarbons of the olefine and higher series, whilst 10% of the petroleum consists of aromatic hydrocarbons belonging to known series, and also a series of hydrocarbons isomeric with styrolene and its isologues. These compounds form brominated derivatives, but no additive compounds; their aromatic character is exhibited in the formation of nitro- and sulpho-derivatives. A petroleum from near Tiflis, examined by Beilstein and Kurbatow (*J. Chem. Soc.*, 1921, **40**, 1020), yielded a fraction of lower b. p. containing the paraffins C_4H_{10} to C_7H_{16}, with a little benzene and toluene. By treating the fraction of a Caucasian petroleum boiling between 180° and 200° with fuming sulphuric acid, Markownikoff and Oglobini found that various sulphonic acids were formed, while the hydrocarbons of the formula C_nH_{2n} were left unchanged. Isomerides of cymene, *m*-methyl-propylbenzene, and probably durene, were present. The 240° to 250° fraction contained a modification of propylnaphthalene ($C_{13}H_{14}$), then $C_{12}H_{14}$ and $C_{11}H_{14}$ (the last probably belonging to the cinnamene series), and finally $C_{15}H_{30}$ (? $C_{15}H_{10}$). The petroleum also contains neutral and acid oxygenated bodies. A petroleum examined by Markownikoff yielded a fraction boiling between 220° and 230°, which contained 5.25% of oxygen.

The investigation of Russian petroleum is very difficult, owing to the facility with which the constituents break up into other substances on distillation, especially during the latter part of the process. When passed through an iron tube heated to bright redness, Caucasian petroleum yields an abundant deposit of carbon, which soon chokes the tube, the metal itself being strongly corroded. The volatile products consist largely of benzene and its homologues, with naphthalene and anthracene. This reaction has been utilised for the production of benzene and anthracene from Russian petroleum.

Galician petroleum, according to Lachowicz, contains a number of paraffins and also aromatic hydrocarbons. Pawlewski found in a petroleum from Kleczany about 2% of aromatic hydrocarbons, consisting chiefly of benzene and *p*-xylene. The fraction boiling between 97° and 100° consists chiefly of heptane with some toluene hexahydride, but the presence of xylene hexahydride was not established. The first six fractions obtained by distilling the crude petroleum on the large scale are not acted on by bromine, but the seventh and higher fractions absorb bromine with evolution of heat. Hence it is probable that olefines do not pre-exist in the petroleum, but are formed during the distillation by the decomposition of paraffins. Hell and Meidinger have isolated from Wallachian petroleum an acid forming alkali salts resembling soft soap. Other homologous acids are probably present.

Galician petroleums, according to R. Zaloziecki and H. Klarfeld (*Chem. Zeit.*, 31, 1155–6, 1170–2), have been found to give the strongest indications of having optically active constituents. Consideration of the optical activity in petroleum is mainly given because of its bearing on the question of its origin. It had been held originally by Engler and others that it had come from animal remains, whilst the discovery of the optical properties of certain petroleums has given strong reasons for the belief that it has had its source from vegetable as well as from animal remains.

Persian petroleum, as now worked by the Anglo-Persian Oil Co. at their Llandarcy refinery in Wales, is a mixed paraffin and asphalt basic oil.

Rangoon tar is a heavy variety of petroleum, of a semi-solid consistency, owing to the presence of about 40% of solid paraffin. By fractional distillation, Warren and Storer proved the presence of the paraffins from C_7H_{16} to C_9H_{20}, olefines from C_9H_{18} to $C_{13}H_{26}$, besides xylene, cumene, and naphthalene.

The composition of petroleums from other sources has been but imperfectly ascertained. The behaviour of some of them on distillation is described later.

DISTILLATION OF PETROLEUM

The method of treating crude petroleum for the manufacture of commercial products varies considerably with the character of the crude article and the practice of the works, but it is always essentially a process of fractional separation by distillation, whether the latter be under normal pressure or under excess pressure for the development of "cracking" the oil taken originally.

In current American practice of oil refining (an epitome of which we take from Cross' Bulletin No. 15 on Petroleum) the oil is placed in horizontal stills holding from 750 to 1200 barrels and heated by direct firing. Under the name of *Benzine* (gasoline and naphtha) is included all of the light distillate which vaporises up to 410° F. The gravity of the total distillate so obtained may vary from 50° Bé. to 64° Bé. according to the different types of crude oil used. In cases where the crude is of good quality it is not necessary to treat the benzine with acid but merely to redistil it with steam coils. When, however, a high sulphur or a low grade petroleum has been used, the distillate is treated in the agitator with sulphuric acid followed by water, sodium hydroxide solution, and final washing and then redistilled in a steam still with dephlegmator to give a gasoline of 58° to 60° gravity.

Kerosene (or "water-white" distillate) comes over just after the crude benzine. In distilling kerosene from the crude, it is desirable to stop before there is discolorisation from decomposition or cracking. Cracking may be very largely prevented and kerosene may be greatly sweetened by using open steam throughout the entire distillation. The "water-white" distillate or first run kerosene is now created with acid and sodium hydroxide in the agitator and exposed to heat, air and light in a shallow tank or bleacher in which all water is settled out.

Solar oil or distillate oil is taken out immediately following the kerosene, being a crude distillate not subjected to refining and sold for use in explosion engines, as a high grade special fuel oil or for cracking stock. The making of this product depends upon the market. It may be about a 36° Bé. gravity product, or it may be combined with gas oil or straw oil.

Gas oil is taken immediately following the distillate oil or kerosene, and its distillation is continued until the residuum in the still has a gravity of 23 to 26° Bé. It is distinctly a destructive distillation, and the yield depends largely upon the method and rate of firing. Gas oil is used in making illuminating gas and contains a considerable amount of olefines and cracked products, and is not refined except for special purposes. It is also used as a cracking stock. By the Burton process or the Cross process, gas oil commercially yields 60 to 65% of gasoline. If a gas oil fraction low in olefines (straw oil) is desired, it is necessary to distil, using open steam and direct fire. Straight firing gives a more fluid residue on account of cracking.

Residuum or tar is sold as **fuel oil,** or it may be used to produce lubricating oil. In the latter case it may be put into tar or tower stills and run down to coke. If the crude oil contains no wax, then the lubricants may be made by vacuum-, steam- or gas-distillation, and the distillate is only filtered through fuller's earth for use.

Wax distillate is collected following the gas oil and furnishes the stock from which lubricating oils and wax are made. Wax distillate usually has a gravity of 30–32° Bé. viscosity 50–80 at 100° F. and a cold test of 55–100° F. The amount from different crudes varies from none up to 35%. About 10% is a usual amount.

The wax distillate is cooled, and the solidified paraffin wax pressed out at a low temperature under a high pressure. The wax-free oil, known as "pressed distillate," is then reduced in a still to the desired viscosity lubricating stock. When reducing, considerable steam is used in the distillation in order to prevent the oil from "cracking" or as stillmen frequently say, from "burning." Heavy benzine, gas oil and light lubricating distillate are obtained as overhead products, the residue being the base for the heavy lubricating oil. The light lubricating distillate contains volatile products, which must be removed. This is performed by reducing, as before, with fire and steam to the viscosity desired.

Refiners frequently manufacture two grades of lubricating oil, a light and a heavy oil. These oils generally have the following tests:

	LIGHT OIL	HEAVY OIL
Gravity	25.0-32.0° Bé.	20.0-27.0° Bé.
Flash point	300-400° F.	375-425° F.
Fire test	400-460° F.	460-500° F.
Viscosity at 100° F.	50-150	200-400
Cold test	10-30° F.	20-35° F.
Colour (N. P. A.)	2	3, dark red

Paraffin wax is also obtained from the wax distillate cut. The wax distillate is cooled to about 5° F. in chillers by means of a cold brine solution. The solidified mass is granulated and carried forward to the presses by a helicoid conveyor. The wax is then separated from the oil by forcing the cooled mass of oil and wax through filter presses under a high pressure, approximately 350 lb. per square inch. The crude wax remains upon the canvas filter and the oil drops into the pan below.

The crude wax, known as "slack wax" is removed from the press and conveyed to a tank where it is melted. The slack wax contains a large percentage of oil, which must be removed. This is done by a process known as "sweating." The "sweaters" are large shallow pans which contain wire screens a few inches above the bottom. Sufficient water is placed in the pan to cover the screen. The melted wax is then pumped on the water and permitted to solidify slowly. When solid, the water is drawn off at the bottom of the pan, the cake of wax being supported by the screen. The temperature of the sweater room is gradually increased by means of steam in closed steam coils.

The oil known as "foots oil" is first separated from the wax followed by the low melting point or "intermediate wax." The wax from the sweater is known as "scale wax." The scale wax usually has a yellow colour, which is removed by treating and filtering. The scale wax is melted and treated with a few pounds of 66° Bé. sulphuric acid, usually with 1 and 3 lb. in succession. The acid is drawn off and the remaining acid in the wax neutralised with 1 to 3° Bé. sodium hydroxide. The alkali is settled from the wax, the temperature being maintained at about 140° F. during the entire process. The melted wax is then filtered through fuller's earth to the desired colour. Wax has a sp. gr. of about 0.9, m. p. of 120 to 140° F. and not more than 1% of oil and moisture.

After the wax distillate has been removed from the crude oil, a fraction containing considerable amorphous wax, known as "wax tailing" distils over. The wax tailings are not passed through the condenser coils, but are permitted to pass directly from the vapour line to a small tank known as the "wax pot." They are of little value, but may be used for cracking stock.

The "cracking" of petroleum oil has become a very important feature in modern oil refining; greatly modifying the yield of valuable products and using the lesser valuable fractions for this purpose.

"Cracking" involves a breaking up of the heavy hydrocarbons of the oil and a production therefrom of more volatile products. This may take place either in the vapour phase or the liquid phase. The processes that have proved profitable are those in which the decomposing effect is accomplished in the liquid phase of the oil. It may take place under atmospheric pressure by the distillation in the pre; sence of a catalyst like the aluminium chloride of the McAfee process, or under excess pressure (80 to 100 lb. pressure) as in the Burton, the Dubbs and other processes. The material submitted to this pressure distillation is either the product of the primary distillation of the crude known as "gas oil" or that called "fuel oil," and the products are "cracked gasoline," separated carbon and gases from the decomposition reaction. A typical gas made in a Burton still showed 82% saturated hydrocarbons (methane and ethane), 8.5% olefines, and 9.5% hydrogen. The cracked gasoline contains relatively more unsaturated hydrocarbons, the olefine content of gasoline made by "cruding" at 80 to 100 lb. pressure being from 21 to 23%. On the other hand, the gasoline made by the use of aluminium chloride is essentially free from olefines.

Of the present American production of gasoline about 25% is the product of cracking, 70% is natural gasoline obtained in distillation of crude and 5% is extracted from natural gas.

ANALYSIS OF CRUDE PETROLEUM

The most important determinations to be made are the specific gravity, the percentage of water and sediment and the distillation record giving the gasoline, kerosene and residuum percentages. Following these, it is desirable for the proper valuation of a crude oil to have the calorific value, the percentages of sulphur, paraffin wax and the asphalt.

The specific gravity is almost universally determined by the hydrometer and expressed in degrees Baumé. The temperature is carefully observed and the reading thus corrected to 60° F. by the aid of the table proposed by the U. S. Bureau of Standards or other authority. The conversion of this Baumé reading into absolute specific gravity is similarly taken from the tables or obtained by the equation sp. gr. $\frac{60^\circ}{60^\circ} = \frac{140}{130 + \text{Bé}^\circ}$.

The specific gravity can also be directly determined by the pycnometer when the temperature is carefully adjusted to 60° F. The Westphal balance is also available for this direct specific gravity determination.

The **percentage of water and sediment** may be determined in one operation by the American Society for Testing Materials methods, using the centrifuge as shown in Fig. 6 (see Cross' Bulletin No. 16, p. 462).

Exactly 50 c.c. of 90% benzol are measured into each of two centrifuge tubes and exactly 50 c.c. of the oil to be tested and then added to each. The centrifuge tubes are tightly stoppered and shaken vigorously until the contents are thoroughly mixed. The temperature of the bath is maintained at 100° F. and the centrifuge tubes are immersed therein to the 100 c.c. mark for 10 minutes. The two centrifuge tubes are then placed in the centrifuge on opposite sides and are whirled at a rate of 1400 to 1500 r.p.m. or the equivalent for 10 minutes. The combined volumes of water and sediment at the bottom of each tube is read and recorded, estimating to 0.1 c.c. if necessary. The centrifuge tubes are then replaced in the centrifuge, again whirled for 10 minutes as before and removed for reading the volume of water and sediment as before. The operation is repeated until the combined volume of water and sediment in each tube remains constant for two consecutive readings.

The preferred form of centrifuge has a diameter of swing (tip to tip of whirling tubes) of 15 to 17 in. and a speed of at least 1500 r p m or the equivalent If the available centrifuge has a diameter of swing varying from these limits, it is run at the proper speed to give the same centrifugal force at the tips of the tubes as that obtained with the preferred form of centrifuge. The proper speed may be calculated from the following formula which represents the diameter of swing (tip to tip of whirling tubes) of the centrifuge used:

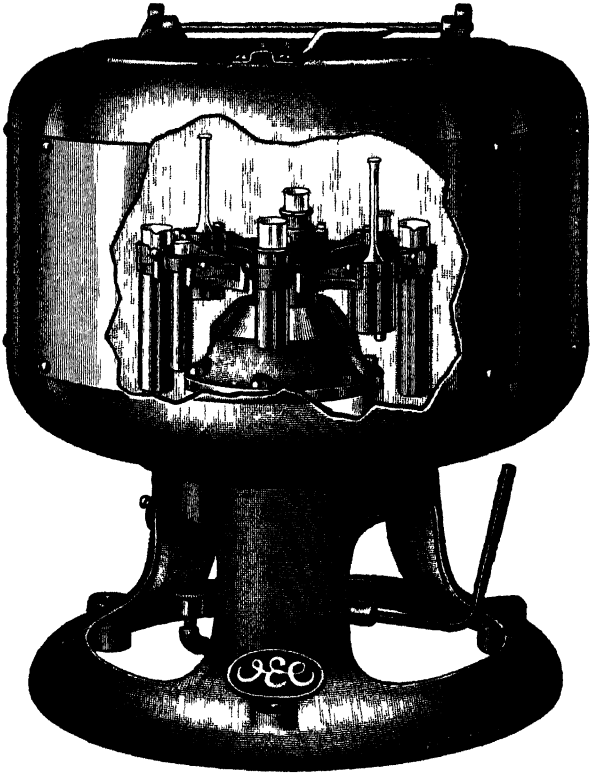

Fig 6—International electric centrifuge with eight place head in position

$$\text{r.p.m.} = 1500\sqrt{\frac{16}{d}}$$

Water.—For water alone in crude petroleum, the distillation method of the A. S. T. M. is more accurate. It is as follows: 100 c.c. of the oil to be tested are measured in an accurate 100 c.c. graduated cylinder at room temperature and poured into the distillation flask. The oil adhering to the walls of the 100 c.c. graduated cylinder is transferred to the distillation flask by mixing with the succession in 25 c.c. portions of gasoline, the cylinder being allowed to drain each time. The sample is taken with great care to see that the water and the oil are uniformly mixed, insuring a representative sample. The apparatus used is that of Dean and Stark (*Methods for Testing Petroleum Products*, Bureau of Mines *Technical Paper* **298,** 35) (see Bureau of Mines No. **298,** p. 30).

The distillation flask is of 500 c.c. size. The oil and gasoline in the distillation flask are thoroughly mixed by twirling the flask with proper care to avoid any loss of material A "boiling stone," such as a piece of unglazed porcelain, may be introduced for the purpose of preventing bumping, during the subsequent distillation. The flask should be of copper or pyrex glass. Heat may be applied by a gas burner or an electric heater The graduated receiver should be kept cool. Distil until no further increase in the volume of the recovered water is observed.

Distillation Analysis of Crude Petroleum.—The method of Engler has been, perhaps, most generally used. The distillation flask (Fig. 84) is shown with the measurements in centimeters. Flasks that do not come up closely to these measurements should be rejected. The bulb of the thermometer[1] is just below the side delivery tube. In making a distillation, wire gauze is used at first as a protection from the flame, but after the lightest fractions have come over it is removed and the distillation carried on with the naked flame, or an asbestos board with a central opening 1¼ in. in diameter may be used. The heat is so regulated that from 2 to 2½ c.c. of distillate pass over per minute. When the first drop falls from the end of the condenser, the reading of the distillation thermometer is recorded as the *initial boiling point.*

In present American practice the distillation of a crude petroleum is carried to 210° (410° F.) before the receiver is changed and this constitutes the *crude gasoline* cut. The distillation is then continued to 300° (572° F.) and this portion is the *kerosene* cut. What remains is *residuum* which may be used as fuel oil or distilled for lubricating oil and wax production. In the distillation of a crude petroleum, if water is present in the oil, some foaming will develop. This can be controlled by careful heating of the upper part of the flask, but before applying heat for this purpose, ·it is necessary to obtain the temperature of the first drop over in the distillation.

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[1] In all distillation tests it is necessary to pay particular attention to the choice of a thermometer. Specifications generally describe the thermometers in detail Such is the case with tests of the A S.T.M. or U. S. Bureau of Mines.

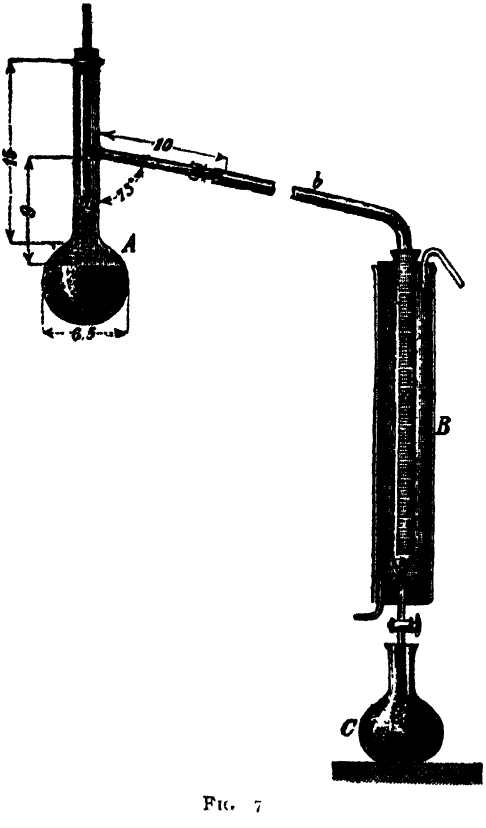

Fig. 7

This distillation of a crude oil will give, as proximate parts, the water, the gasoline, the kerosene and the residuum fractions.

What is termed a **fractional gravity distillation analysis** of crude petroleum may also be carried out, using a Claisen distilling flask of heavy pyrex glass. This form of flask has a large side tubulum bending upward for the insertion of a thermometer and connecting with the condenser. The other neck of the flask is fitted with a glass tube which goes to the bottom of the flask and also with a total immersion thermometer. Five per cent. fractions are collected in graduated cylinders, so that amounts can be measured and specific gravities determined.

Dephlegmators or fractioning columns are sometimes used to secure a more complete separation of the constituents of petroleum. Whilst it is true that they do serve this purpose if well constructed, it is probably better for the sake of uniformity to adhere to the method, just described. Uniform results can be obtained with a standard Engler distillation bulb in the hands of different operators. Dephlegmators differ in construction, and differences in operation have large influence upon the results obtained with their use.

Sp. gr. tests of fractions are made by means of a pycnometer or Sprengel tube (if the amount is small).

The loss to sulphuric acid (degree of unsaturation) may also be determined in the gasolene and kerosene fractions.

Determination of the Calorific Value.—While some authorities recommend the calculation from the results of an ultimate analysis, it is probably best to make a direct determination in a standard form of calorimeter, such as the Mahler, Atwater, Parr and Emerson bombs. The operation of these instruments is detailed in various works on fuels.

Of course, full directions for use are supplied with each instrument. The Rawle (*J. Soc. Chem. Ind.*, 1907, **26,** 665) instrument has been gaining favour in England, as being specially adapted for liquid fuels. A cut accompanies the article.

To convert B.t.u. per pound to calories per grm., multiply by five-ninths. To obtain the water evaporation power, multiply the B.t.u. per pound by 1.035 and divide by 1000. To obtain the B.t.u. per gallon, multiply the B.t.u. per pound by the weight per gallon.

Estimation of Sulphur.—The standard method for the estimation of sulphur in crude petroleum has been, and probably still is, the method of Carius. It consists in oxidising the entire sample of oil with fuming nitric acid in sealed tubes of hard glass at temperatures around 200°. This method is often found very troublesome due to the bursting of tubes. Several other methods give practically identical results if properly carried out, but at the same time the method of Carius will always be the standard method. A brief description of the method is given on page 192.

The only other method that can be considered practically as reliable as that of Carius is the combustion of the oil in a bomb calorimeter.

The estimation may be made at the same time as a determination of calorific value.

Place 20 c.c. of distilled water in the bottom of the bomb. Use 0.5 to 1.0 grm. of oil, weighed into the sample cup of the bomb, when the material is not volatile. For volatile materials use either a small gelatin capsule or a very small glass bulb of the type used in the ultimate organic analysis of such liquids. If the latter is used, place a few drops of sulphur-free alcohol in the sample cup to start combustion. Arrange the ignition mechanism and close the bomb tightly. Admit oxygen until a pressure of 35 to 40 atmospheres is reached. The higher pressure is preferable.

Ignite. Place the bomb in cold water for 20 minutes. Shake vigorously for 25 seconds and allow it to drain for five minutes. Release the pressure rather slowly and open the bomb. Using distilled water in a wash bottle with a very fine jet, wash the wires and cover thoroughly, allowing the washings to collect in the bomb. In the same way wash the sample cup held by small tongs. Transfer the solution from the bomb to a 500 c.c. beaker and wash the inside of the bomb thoroughly. The total volume of solution thus obtained need not exceed 350 c.c. Avoid any loss of material by spattering or otherwise in the various washings.

Filter the solution through a washed filter paper into another beaker, of smaller size if possible. Wash the filter thoroughly. Add the 2 c.c. of hydrochloric acid (sp. gr. 1.20) and 10 c.c. of saturated bromine water. To the hot solution add 10 c.c. of a 10% barium chloride solution, as hot as possible, in a very fine stream or dropwise, so that 30 to 45 seconds are required. Stir vigorously with a glass rod during this addition and for four minutes afterwards. Allow the precipitate to settle for one hour on a steam bath. Cool and let it stand for at least one hour at room temperature. Filter carefully through a suitable ashless filter paper and wash the precipitate with hot water, first by decantation and then on the filter till free from chloride. Transfer the wet filter paper and precipitate to a weighed platinum crucible. Dry carefully over a low flame. Allow the filter paper to burn away and then ignite until the precipitate is just burned white. Cool in a desiccator and weigh. From the increase in weight which is barium sulphate, calculate the percentage of sulphur as follows:

$$\text{Percentage of sulphur} = \frac{\text{grm. of Ba SO}_4 \times 13.734}{\text{grm. of oil used}}$$

Methods that are more suited for rapid routine work are those of Mabery an adaptation of the Burton-Sauer method, and one S. S. Sadtler has found useful in certain cases. The Mabery method (*Proc. Amer. Acad.*, 1896, **31**, 1) consists in burning the substance contained in a porcelain boat in a current of air or oxygen, which enters the combustion tube containing the boat by a small tube of hard glass which is continued beyond the boat to a restriction about midway in the tube. Air also enters the combustion tube through another tube passing in a little beyond the double-bored stopper that carries the longer tube. This air carries oil vapours, which come from the oil due to heat applied carefully below the boat, to the restriction where they meet the main body of air. Beyond the restriction the tube is heated to redness. The sulphur is burned to sulphur trioxide which is absorbed in a dilute sodium hydroxide solution contained in a large U-tube partly filled with glass beads. It is rather difficult to get a proper adjustment of rates of flow, temperatures, etc., unless a person has worked with the method quite a while, and the reviser of the previous edition found that more ready combustion could be obtained if a wad of platinised asbestos were placed ahead of the constriction or, better yet, between two of them, leaving space an inch in length. This catalyser causes an intensely hot spot, locally, where the oil vapours and the air meet, and Sadtler was able in that way to burn Texas oils, which otherwise seemed to be very difficult to burn by the ordinary Mabery-Burton-Sauer method. This difficulty seemed to be due to the force of gas caused by the rather sudden liberation of hydrogen sulphide from the action of sulphur on some of the hydrocarbons, when the proper temperature was reached.

A different method brought out by S. S. Sadtler (*J. Amer. Chem. Soc.* 1905, **27**, 1188), known as the double crucible method, is found very useful for determining sulphur in crude oils and residuums which contain sulphur in excess of 1%. It has been found satisfactory for analysing Texas and other sulphur-containing crudes, and compares favourably with the Carius method.

The crucible is shown in Fig. 8.[1] The substance is first weighed into the inner crucible, which is placed open end up on the balance pan. About 1 grm. of sulphur compound containing 1% sulphur is taken.

Enough Eschka mixture is then put in to absorb the substance, if a liquid, or mixed with it in any case, and the crucible is then filled to the top with moderate tamping.

Freshly ignited white asbestos (*a*) is then put around the raised portion of the bottom of the outer crucible to keep the two crucibles from being in actual contact. It is next lowered over the inner crucible and then both crucibles inverted. Eschka mixture is then put in between the crucibles. The outer crucible is then put through a hole in a piece of thin but firm asbestos board so that very little, if any, of the sides can be exposed to the direct action of the flame.

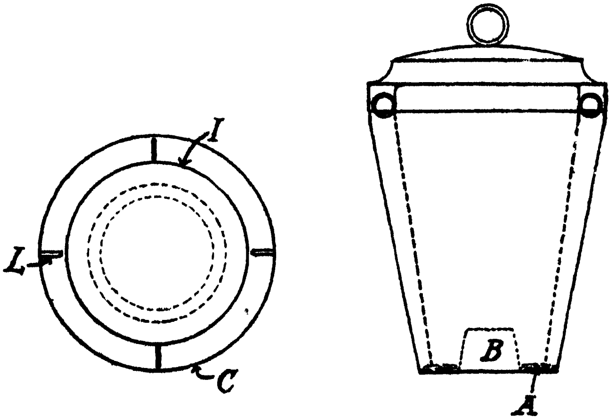

FIG. 8.—Sadtler double crucible.

The outer crucible is made with straight sides like an inverted truncated cone.

A very small pointed flame of a Bunsen burner is now used so that the flame is chiefly in the indentation on the bottom (*B*). If gases do not come off from the crucible in three to five minutes with this flame, the heat is increased, and when no more odour is noticeable the crucible is placed in a piece of asbestos having a larger hole, so that half of the crucible may become red-hot and is kept so for 10 minutes. The flame is then withdrawn, and when cool the inner crucible is carefully raised and tapped, so that its contents are dropped into the outer one, when the carbon is burned out with a shield of asbestos to protect the contents from the sulphur gases of the flame.

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[1] Cut reproduced from *J. Amer. Chem. Soc.* with permission.

The contents of the crucibles are then washed into a beaker. Bromine is added to oxidise sulphites, etc., the solution is filtered, acidified and precipitated with barium chloride as in the case of determinations of sulphur in coal.

Estimation of Paraffin in Crude Petroleums.– Taking 100 grm. of crude petroleum in a tubulated glass retort, quickly distil off all up to 300° (thermometer in vapour). Then, changing the receptacle, collect the remaining distillate in a weighed flask, using no condenser, and continue the distillation without thermometer until coking of the residue. By again weighing the receptacle, the total weight of the heavy oil which is distilled over is determined, from which the percentage of paraffin found can be calculated back to the original crude oil taken. 5 to 10 grm. of this heavy oil distillate are then to be dissolved, at room temperature, in a mixture of 1 part ether and 1 part alcohol, until a clear solution is obtained. Then cool down with the aid of an ice mixture until a temperature of –20° is obtained. Add, in addition, so much of the mixture of alcohol and ether, until all the oily portions remain dissolved at –20°, and only paraffin flakes are visible. These latter are then to be transferred to a small filter, surrounded by a cooling mixture of ice and salt kept at a temperature of –20° as shown in Fig. 9, the liquid

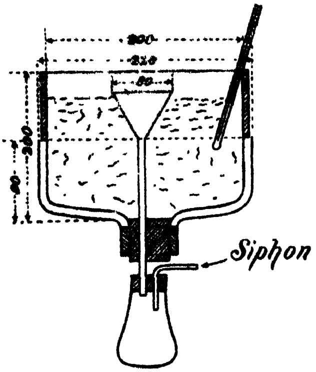

FIG. 9.—Ice-cooled paraffin filter.

being drawn off by connection with a suction pump, the separated paraffin on the filter being washed with previously cooled alcohol-ether mixture, until no oily portion shows in the washings. The precipitate is then taken from the ice mixture, dissolved off of the filter into a tared glass dish, with the aid of warm benzine, the benzine being then carefully evaporated over the water-bath. If, on cooling the dish, it is found that the paraffin is of hard variety, it is dried for 15 minutes at 105°, and, after cooling in the desiccator, weighed. If, on the other hand, the residue is soft paraffin, melting under 45°, this is best dried by keeping it in a vacuum desiccator at a temperature of 50°, and then weighing. To the weighed amounts of paraffin so obtained is to be added, because of the slight solubility of paraffin in the alcohol-ether mixture, 0.2% when the distillate is perfectly liquid, .4% in the case of distillates which show a separation of solid material at 15°, and 1% in the case of solid distillate masses.

With these corrections, the estimation is regarded as accurately representing paraffin in crude oils and in lubricating oils. For such petroleums as contain both paraffin and asphalt base, the modification made by Clifford Richardson (*J. Soc. Chem. Ind.*, 1902, **21**, 690) is to be used.

Estimation of Asphalt in Petroleum.—The method proposed by Holde has been generally adopted. 5 grm. of crude oil are shaken in an Erlenmeyer flask with 220 c.c. of petroleum spirit (paraffin-base petroleum naphtha 88° B.); in the case of oils poor in asphalt, 5–20 c.c. of oil are taken. After standing for at least a day, the clear liquid is decanted through a small pleated filter. The bulk of the precipitate is brought on the filter, and the flask and filter are washed with the solvent until the filtrate no longer leaves an oily residue on evaporation. The asphalt on the filter is then dissolved by means of hot benzene, the solution concentrated by distillation, the remainder washed into a weighed dish, and the solid residue, after evaporation and drying at 100°, weighed. This procedure leaves any non-asphaltic matter which may have been precipitated by petroleum spirit on the filter; this may be estimated separately.

Formolite Number.—The only other test which is at times applied to crude petroleum is the determination of the **formolite number.** This is claimed to be specific for straight-chain olefines which give a brown syrupy liquid and for closed-chain olefines and for aromatic hydrocarbons which yield solid polymerization products ("formolite"). By the method of Marcusson, 27 grm. of the oil are dissolved in 50 c.c. of petroleum spirit (previously treated with sulphuric acid and formaldehyde), 30 c.c. of concentrated sulphuric acid are added and the mixture is cooled in ice water. 15 c.c. of formaldehyde then are added and the mixture is shaken with cooling until heat ceases to be evolved, after which it is added to 200 c.c. of ice water. Next the whole is neutralised with ammonia in excess and finally the precipitate is collected on a Büchner funnel, washed first with naphtha and then with water, dried at 105°, cooled and weighed. The formolite number is the number of grams of dried precipitate from 100 c.c. of the oil.

LIGHT NAPHTHA AND GASOLINE PRODUCTS

Pentane.—With the exception of methane, which exists in a fairly pure state in natural gas, pentane in perhaps the only other single constituent of petroleum that is obtained from it and used commercially. Normal pentane boils at 36.3°, and so can only be kept at ordinary temperatures in sealed cans, etc. Pentane is burned in the pentane lamp used in photometry. According to C. O. Bond (*J. Frank. Inst.*, 1908, **165**, 189–209) the following methods are adopted in preparing pure pentane and testing it.

Light American petroleum, such as is known as gasoline and used for making air gas, is to be further rectified by 3 distillations, at 55°, 50° and 45° in succession. The distillate at 45° is to be shaken up from time to time, during 2 periods of not less than 3 hours each, with $\frac{1}{10}$ its volume of (1) strong sulphuric acid, and (2) a solution of sodium hydroxide. After these treatments it is to be again distilled, and that portion of it to be collected for use which comes over between the temperatures of 25° and 40°. It will consist chiefly of pentane, together with small quantities of lower and higher homologues whose presence does not affect the light of the lamp.

Testing Pentane.—The sp. gr. of the liquid pentane at 15° should not be less than 0.6235 nor more than 0.626 as compared with that of water of maximum density. The density of the pentane when gaseous, as compared with that of hydrogen at the same temperature and under the same pressure, may be taken. This is done most readily and exactly by Gay Lussac's method, under a pressure of about half an atmosphere, and at temperatures between 25° and 35°. The density of gaseous pentane should lie between 36 and 38, hydrogen being taken as 1.

Any admixture with pentane, of hydrocarbons belonging to other groups and having photometric value—such as benzene or amylene—must be avoided. Their presence may be detected by the following test: Bring into a white stoppered glass bottle of from 80 c.c. to 100 c.c. capacity, 10 c.c. of nitric acid, sp. gr. 1.32 (made by diluting pure nitric acid with half its bulk of water). Add a few drops of a dilute solution of potassium permanganate, sufficient to give to the acid a full and permanent pink colour. Pour into the bottle 50 c.c. of the sample of pentane, and shake strongly from time to time during 5 minutes. If no hydrocarbons other than paraffins are present, the pink colour, though somewhat paler, will still be distinct. If there is an admixture of as much as 0.5% of amylene or benzene, the colour will have disappeared.

Purified Petroleum Benzine (*Benzinum Purificatum of the United States Pharmacopœia*).—Add 60 c.c. of sulphuric aid to 550 c.c. of water, and when the mixture has become cold, pour it into a bottle having the capacity of about 2 litres. Add 8 grm. of potassium permanganate and agitate until it is dissolved, then add the petroleum benzine, in 4 portions of 250 c.c. each, shaking the liquid after each addition. Allow the liquids to remain in contact for 24 hours, shaking the bottle at frequent intervals; then decant the petroleum benzine into another bottle of the same capacity, and having dissolved 2 grm. of potassium permanganate in 240 c.c. of water, in which 2 grm. of sodium hydroxide has previously been dissolved, mix the liquids and agitate the mixture frequently during several hours, then decant, repeat the washing with water, and again decant the purified petroleum benzine.

On evaporating 10 c.c. of purified petroleum benzine from a piece of clean filter-paper, no greasy stain should remain, and the odour should not be disagreeable or notably sulphuretted; no residue should be left upon evaporating purified petroleum benzine from a warmed dish (absence of heavy hydrocarbons).

When it is boiled for a few minutes with 0.25 its volume of spirits of ammonia and a few drops of silver nitrate T. S., the liquid should not turn brown (absence of pyrogenous products and sulphur compounds).

It is described as "a clear colourless, non-fluorescent volatile liquid, of an ethereal or faint petroleum-like odour and having a neutral reaction. It is highly inflammable and its vapour when mixed with air and ignited explodes violently.

"It is practically insoluble in water; freely soluble in alcohol, and miscible with ether, chloroform, benzene, volatile oils and fixed oils with the exception of castor oil."

The tests of the U. S. P. for *Benzinum* are: Sp. gr., 0.638 to 0.660 at 25°; b. p., 40° to 80°. If 5 drops of petroleum benzine be added to a mixture of 40 drops of sulphuric acid and 10 drops of nitric acid, in a test-tube, the liquid warmed for about ten minutes, and then set aside for half an hour on diluting it in a shallow dish with water, it should not evolve the bitter almond like odour of nitrobenzene (difference from, and absence of, *benzene*).

	Petroleum spirit	Shale naphtha	Coal-tar naphtha
Chemical composition.	Contains at least 75% of paraffins, principally heptane, the remainder apparently olefines, with traces of aromatic hydrocarbons.	Contains at least 40 to 50% of olefines, principally heptene; the remainder paraffins. No trace of aromatic hydrocarbons.	Consists almost wholly of benzenes. A small percentage of open-chain hydrocarbons in some samples.
Sp. gr. at 15°	0.700	0.718	0.876
Chiefly distils between	65° and 100°.	65° and 100°.	80° and 120°.
Solvent action on coal-tar pitch.	Very slight action; liquid but slightly coloured even after prolonged contact.	Behaves similarly to petroleum spirit.	Readily dissolves pitch, forming a deep brown solution.
Behaviour on shaking 3 volumes of the sample at 20° with 1 volume of fused crystals of absolute phenol.	No apparent solution; the liquids are not miscible, but set to a mass of crystals when cooled slightly below 0°.	The liquids form a homogeneous mixture, often setting to a mass of crystals at 18° to 20°.	The liquids form a homogeneous mixture.
Reaction with bromine in the cold.	Combines with 10 to 20% of its weight of bromine.	Combines with upward of 60% of its weight of bromine.	Reacts slowly with a considerable proportion of bromine.

The "petroleum benzine" of the German Pharmacopœia is the colourless, non-fluorescent portions of petroleum, having a sp. gr. of 0.640 to 0.670, and distilling almost entirely between 55° and 75°.

On adding 2 c.c. of this liquid to a cold mixture of 1 c.c. of sulphuric acid and 4 c.c. of fuming nitric acid and shaking, no appreciable colour and no odour of bitter almonds should be produced.

The British Pharmacopœia (1898) defines "petroleum spirit" as a derivative of petroleum, boiling between 50° and 60°, and with a sp. gr. between 0.670 to 0.700.

Water cannot exist in notable quantity in petroleum spirit without rendering the liquid milky. If present to an extent sufficient to be thus visible, the liquid is rendered unfit for burning in sponge lamps, etc. The water may be removed by prolonged subsidence, or more rapidly and perfectly by agitating the sample with a little dry plaster of Paris.

Shale naphtha, which is the lighter and more volatile portion of the oil obtained by the distillation of bituminous shale, is a product very similar to petroleum spirit in most of its properties and uses. Allen found, however, that the shale naphtha presents certain differences, which are due to a much larger proportion of olefines than exist in petroleum naphtha. The table on page 93 exhibits concisely these differences, and compares the characters of a sample of coal-tar naphtha with specimens of similar products from shale and American petroleum. Variation in minor details will be met with in different samples from similar sources. (See Crude Shale Oil, page 36.)

EXAMINATION OF NAPHTHA AND GASOLINE

The tests of importance are here somewhat different from those described for crude petroleum, although several of the tests already described are also applicable.

Specific Gravity.—As before noted under crude petroleum, three methods are available; the hydrometer method, the use of the pycnometer or sp. gr. bottle and the use of the Westphal balance. Of these, the first is the method generally used because of convenience. Of course, accurate sp. gr. spindles calibrated for the Baumé scale for liquids lighter than water and with attached thermometer are to be used. If the temperature of the gasoline is other than 60° F., the observed Baumé reading must be corrected to 60° F. by means of an accurate set of tables, such as those prepared and published by the Bureau of Standards (*Circular*, 57). Where time allows, it is more accurate to make the determination with the liquid at a temperature of 60° F. exactly. A convenient method for doing this is first to place the cylinder in water at a temperature of 60° F. and after cooling the gasoline to a temperature of 60° F. to pour it into the cylinder and then insert the hydrometer. If the temperature of the water has risen in the meantime, flow in ice water until the temperature is again at 60° F. Finally stir the gasoline until it is at 60° F. and after a few seconds read the hydrometer.

For direct determination of absolute sp. gr. figures, the Westphal balance furnishes a convenient means, as it is adjusted to 60° F. and the sample can be cooled to that temperature as above described.

For the distillation test, the Bureau of Mines method (which is slightly modified from the American Society for Testing Materials Method) is used. The Engler flask and condensing arrangement is that shown already on page 84. In this case the bath around the condenser is filled with cracked ice and enough water added to cover the condenser tube, the object being to maintain a temperature between 32° F. and 40° F. The bulb of the distillation thermometer is covered uniformly with long fibre absorbent cotton, which is taken fresh for each distillation, the object being to prevent fluctuations of temperature.

In this gasoline distillation, the distilling bulb and burner under it are enclosed in a square dish or box of thin sheet metal with a door on one side and several draft holes near the bottom.

One hundred c.c. of the gasoline are measured into the 100 c.c. graduated cylinder, the gasoline and cylinder being both cooled to a temperature between 55° F. and 65° F. and is transferred direct to the Engler flask using a long stemmed funnel with a small flare so that no liquid is permitted to flow into the vapour tube.

The thermometer provided with a cork is fitted into the flask so that it will be in the middle of the neck and so that the lower end of the capillary tube is on a level with the inside of the bottom of the vapour outlet at its junction with the neck of the flask. The position of the flask shall be so adjusted that the vapour tube extends into the condenser tube not less than 1 in. nor more than 2 in.

The graduated cylinder which has previously been used in measuring the charge, is placed without further draining at the outlet of the condenser tube in such a position that the condenser tube shall extend into the graduate at least 1 in. but not below the 100 c.c.

mark. If the room temperature is above 65° F., the cylindrical graduate shall be immersed up to the 100 c.c. mark in a glass water bath maintained at a temperature between 55° F. and 65° F. The top of the graduate is losely covered with a piece of fibre blotting paper or similar material so that it fits the condenser tube tightly. Heat is applied at a uniform rate so that the first drop falls from the condenser in not less than 5 nor more than 10 minutes.

When the first drop falls from the end of the condenser, the reading of the distillation thermometer is recorded as the *Initial Boiling Point.* The receiving cylinder is then moved so that the end of the condenser tube shall touch the side of the cylinder. Heat is then regulated so that distillation proceeds at a uniform rate of not less than 4 or more than 5 c.c. per minute. The reading of the distillation thermometer is recorded when the bottom of the meniscus of the distillate in the receiving graduate is at each 10 c.c. mark or if desired, also at each 5 c.c. mark.

After the 90% point has been recorded, the heat may be increased sufficiently to bring over the heavy ends. The heating shall be continued until the mercury reaches a maximum and then starts to fall consistently.

The highest temperature observed shall be recorded as the *end point* or maximum temperature. This point will be reached when the bottom of the flask has become dry. The total volume of distillate collected in the receiving flask is recorded as the *total recovery.* The cooled residue in the Engler flask is poured into a cylindrical graduate and the volume is recorded as *residue.* The difference between the 100 c.c. taken and the sum of the recovery and the residue is calculated and recorded as *distillation loss.*

Unsaturated hydrocarbons in a gasoline sample are estimated by a test with sulphuric acid. Weigh a clean and dry Babcock cream bottle of which the neck is so graduated that at least 5 c.c. may be read off. Add exactly 5 c.c. of the oil to be tested. Weigh again, giving the amount of oil used. Cool in ice water and add 10 c.c. of concentrated commercial sulphuric acid, letting the acid run down the sides of the bottle. Shake while cooling in the ice water. Keep stoppered with a rubbor stopper. Let it stand for one-half hour with occasional shaking and constant cooling. Add sufficient concentrated commercial sulphuric acid to bring the reading to about the top of the scale on the neck of the bottle. Centrifuge 5 minutes at a speed of 1,000 r.p.m. Keep the rubber stopper in while centrifuging so that there will be no evaporation. Care should be taken that the stopper be large enough so that it is not forced into the bottle. The reading in the neck of the bottle divided by 5 is the net amount of saturated hydrocarbons contained. This, multiplied by 20 and taken from 100, gives the percentage of unsaturated hydrocarbons.

"Doctor" Test for Gasoline.—Sodium plumbite or "doctor" solution—dissolve 125 grm. of sodium hydroxide in a litre of distilled water. Add 70 grm. of litharge and shake vigorously for 15 or 30 minutes or let it stand with occasional shaking for at least a day. Allow it to settle and decant off the clear liquid. Filtration through a mat of asbestos may be employed if the solution does not settle clear. The solution should be kept in a bottle tightly stoppered. Shake vigourously for about 15 seconds 2 volumes of gasoline and 1 volume of the "doctor" solution. Note colour. A small pinch of flowers of sulphur should be added, and the tube again shaken for 15 seconds and allowed to settle. The quantity of sulphur used should be such that practically all of the sulphur floats on the surface, separating the gasoline from the "doctor" solution.

If the gasoline is discoloured or if the sulphur film is so dark that its yellow colour is noticeably masked, the test shall be reported as positive, and the gasoline condemned as "sour." If the liquid remains unchanged in colour and if the sulphur film is bright yellow, or only slightly discoloured with gray or flecked with black, the test shall be reported negative and the gasoline considered sweet.

A test of importance now applied to gasoline is *the corrosion and gumming test.* The apparatus used in this test consists of a freshly polished hemispherical dish of thin copper, approximately 3½ in. in diameter.

Fill this dish within ⅜ in. of the top with the gasoline to be examined and place the dish on a steam bath. Leave the dish on the steam bath until all volatile portions have disappeared.

If the gasoline contains any elementary sulphur in solution, the bottom of the dish will be blackened.

If the gasoline contains undesirable gum-forming constituents, there will be a weighable amount of gum deposited on the dish.

U. S. SPECIFICATIONS FOR GASOLINE

(Technical Paper 298 Bureau of Mines)

Aviation Gasoline, Domestic Grade

General.

1. This specification covers the grade of gasoline used by the United States Government and its agencies for aviation fuel where the fighting grade is not required.

2. The gasoline shall be free from undissolved water and suspended matter.

Properties and Tests.

3. Colour: The colour shall not be darker than 25 Saybolt.

4. Doctor Test: The doctor test shall be negative.

5. Corrosion Test: 100 c.c. of the gasoline shall cause no gray black corrosion and no weighable amount of deposit when evaporated in a polished copper dish.

6. Unsaturated hydrocarbons: not more than 2.0% of the gasoline shall be soluble in concentrated sulphuric acid.

7. Distillation range:

When 5% of the sample has been recovered in the graduated receiver, the thermometer shall not read more than 75°. (167° F.) or less than 50° (122° F.).

When 50% has been recovered in the receiver, the thermometer shall not read more than 105° (221° F.).

When 90% has been recovered in the receiver, the thermometer shall not read more than 155° (311° F.).

When 96% has been recovered in the receiver, the thermometer shall not read more than 175° (347° F.).

The end point shall not be higher than 190° (374° F.).

At least 96% shall be recovered as distillate in the receiver from distillation.

The distillation loss shall not exceed 2% when the residue in the flask is cooled and added to the distillate in the receiver.

8. Acidity: The residue remaining in the flask after the distillation is completed shall not show an acid reaction.

All tests shall be made according to the methods for testing gasoline adopted by the Interdepartmental Petroleum Specifications Committee.

Motor Gasoline ("New Navy")

General.

1. This specification covers the grade of gasoline used by the United States Government and its agencies as a fuel for automobiles, motor boats and similar engines.

2. The colour shall be not darker than No. 16 Saybolt.

3. A clean copper strip shall not be discoloured when submerged in gasoline for 3 hours at 122° F.

Properties and Tests.

4. Distillation range.

When the first drop has been recovered in the graduated receiver, the thermometer shall not read more than 60° (140° F.).

When 20% has been recovered in the receiver, the thermometer shall not read more than 105° (221° F.).

When 50% has been recovered in the receiver, the thermometer shall not read more than 140° (284° F.).

When 90% has been recovered in the receiver, the thermometer shall not read more than 190° (374° F.).

The end point shall not be higher than 225° (437° F.).

At least 95% shall be recovered as distilled in the receiver from the distillation.

All tests shall be made according to the methods for testing gasoline adopted by the Interdepartmental Petroleum Specifications Committee.

KEROSENE, COAL OIL, ILLUMINATING OIL, BURNING OIL

Kerosene in a general way may be defined as that fraction of crude petroleum or oil made by the pyrogenic decomposition of shales or coal which distils at a temperature of from 302° F. to 572° F., (150–300°) and contains no gasoline or residuum. Its flash-point is always greater than 100° F. and usually greater than 120° F. Its colour may be standard-white, prime-white, superfine-white or water-white. Its gravity ranges from 31° to 48° Bé. Typical kerosene has a gravity of 41 to 42° Bé. Sulphur is usually almost completely absent from kerosene, being less than 0.03%. It consists chiefly of the paraffin series, particularly when the gravity is greater than 38°. The principal constituents are nonane, decane, undecance, duodecane, tridecane, tetradecane, pentadecane, hexadecane and heptadecane. With lower gravities it contains naphthenes and aromatic compounds. This is particularly true of Louisiana oils and California oils.

The standards for good kerosene have been found to be within the following limits:

1. Sp. gr. is between 0.760–0.860 (54.2–32.8° Bé.).
2. Flash-point is over 100° F. by closed tester.
3. Colour is "water-white" with no turbidity.
4. Cold test is below 10° F.
5. End point is below 600° F.
6. Sulphur is below 0.05%.
7. Acid is absent.
8. It does not lose more than 1% on treatment with 66° sulphuric acid.
9. It burns without incrustation or smoking in an ordinary kerosene lamp.

The following are the characters and special applications of certain other varieties of mineral burning oils:

Mineral Sperm Oil.—Sp. gr. 0.829 to 0.847. Abel flash-point 115.5° (240° F.); fire-test about 148.8° (300° F.). Specially adapted for lighthouse and locomotive lights. Its use is compulsory on some of the American railroads, and it is also extensively employed on board ship. "Mineral colza oil" and "mineral seal oil" are similar products.

Belmontine Oil.—Obtained by distillation of Rangoon tar or Burmese petroleum with superheated steam. Sp. gr. 0.847; fire-test 56.6° (134° F.). Though heavy, the oil has but little viscosity, and will rise through a long wick. The flame is very white, and of high illuminating power.

Solar oil is a name commonly applied in Russia to an intermediate oil of about 0.860 sp. gr., and flashing at about 104.4° (220° F.) by the Abel test.

Photogene Oil from shale resembles refined petroleum in all essential physical respects; but, when examined by the bromine method, the shale product is found to contain a smaller percentage of paraffins and more olefines than is the case with petroleum. Some samples of shale photogene contain only 5 or 6% of paraffins. S. S. Sadtler has frequently found that when 3 volumes of petroleum kerosene were shaken with one of fused crystals of absolute phenol, the latter gradually assumed a dark violet, and ultimately a black, colour, but the reaction is not invariably produced; and no such reaction was observed to occur with burning oil from shale. The mixture of petroleum kerosene and phenol becomes turbid at 42° to 49°, but the shale oil mixture remains clear until the temperature has fallen to about 25° F.

EXAMINATION OF KEROSENE OR ILLUMINATING OILS

The determinations usually made are: sp. gr., flash and burning point; colour; distillation test; sulphur; "doctor" test; and flow test.

Sp. Gr.—This has been already described and explained under the Analysis of Gasoline and Light Naphtha.

Flash Point of Kerosene and Other Volatile Inflammable[1] Liquids. (With standard "tag" closed tester.) The test must be performed in a dim light so as to see the flash plainly. Surround the tester on three sides with an inclosure to keep away drafts. A shield about 18 in. square at base and 2 ft. high, open in front, is satisfactory. See that tester is firm and level. For accuracy, the flash-point thermometers which are especially designed for the instrument should be used, as the position of the bulb of the thermometer in the oil cup is essential. Put the water-bath thermometer in place. Place a receptacle under the overflow spout to catch the overflow. Fill the water bath with water at such a temperature that when testing is started, the temperature of the water bath will be at least 10° below the probable flash-point of the oil to be tested. Put the oil cup in place in the water bath. Measure 50 c.c. of the oil to be tested in a pipette or a graduate and place in oil cup. The temperature of the oil must be at least 10° below its probable flash-point when testing is started. Destroy any bubbles on the surface of the oil. Put on cover with flash-point thermometers in place and gas tube attached. Light pilot light on cover and adjust flame to size of the small white bead on cover.

Light and place the heating lamp, filled with alcohol in base of tester and see that it is centrally located. Adjust flame of alcohol lamp so that temperature of oil in cup rises at the rate of about 1° (1.8° F.) per minute or not faster than 1° (1.8° F.) nor slower than

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[1] This is essentially in accordance with the method of the American Society for Testing Materials, Book of Standards, 1921, 669, and is prescribed by them for all volatile flammable liquids flashing below 175° F., with the exception of fuel oil.

0.9° (1.6° F.) per minute. Record the "time of applying the heating lamp," record the "temperature of the water bath at start," record the "temperature of the oil sample at start." When the temperature of the oil reaches about 5° below the probable flash-point of the oil, turn the knob on the cover so as to introduce the test

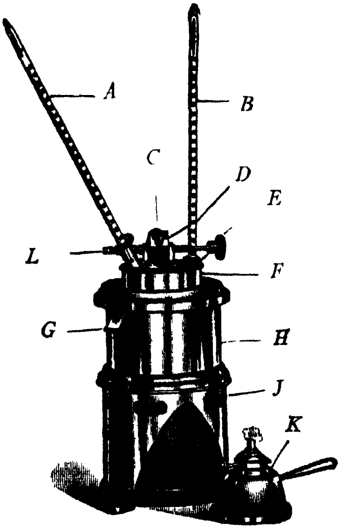

FIG. 10.

(*A*) Thermometer, indicating the temperature of the oil.

(*B*) Thermometer, indicating the temperature of the water-bath.

(*C*) A miniature oil well to supply the test flame when gas is not available, mounted on the axis about which the test flame burner is rotated which axis is hollow and provided with connection of one end for gas hose, and provided also with needle valve for controlling gas supply, when gas is available, the gas passing through the empty oil well.

(*D*) Gas or oil tip for test flame.

(*E*) Cover for oil cup, provided with three openings, which are in turn covered by a movable slide operated by a knurled hand knob, which also operates the test flame burner in unison with the movable slide, so that by turning this knob, the test flame is lowered into the middle opening in the cover, at the same time that this opening is uncovered by the movement of the slide.

(*F*) Oil cup (which cannot be seen in the illustration), of standardised size, weight and shape, fitting into the top of the water bath.

(*G*) Overflow spout.

(*H*) Water bath, of copper, fitting into the top of the body, and provided with an overflow spout and openings in its top, to receive the oil cup and water bath thermometer.

(*J*) Body of metal, attached to substantial cast metal base provided with three feet.

(*K*) Alcohol lamp for heating the water bath.

(*L*) Gas hose.

flame into the cup and turn it promptly back again. Do not let it snap back. The time consumed in turning the knob down and back should be about one full second, or the time required to pronounce distinctly the words "one thousand and one." Record the "time of making the first introduction of the test flame" and record the "temperature of the oil sample at time of first test." Repeat the application of the test flame at every 0.5° rise in temperature of the oil until there is a flash of the oil within the cup. Do not be misled by an enlargement of the test flame or halo around it when it has entered into the cup or by slight flickering of the flame; the true flash consumes the gas in the top of the cup and causes a very slight puff. Record the "time at which the flash-point is reached," and the "flash-point." If the rise in temperature of the oil from the "time of making the first introduction of the test flame" to the "time at which the flash-point is reached" was faster than 1.1° or slower than 0.9°, per minute, the test should be questioned and the alcohol heating lamp adjusted so as to correct the rate of heating. It will be found that the wick of this lamp can be so accurately adjusted as to give a uniform rate of rise in temperature of 1° per minute and remain so.

Repeat Tests.—It is not necessary to turn off the test flame with the small regulating valve on the cover; leave it adjusted to give the proper size of flame.

Having completed the preliminary test, remove the heating lamp, lift up the oil cup cover and wipe off the thermometer bulb. Lift out the oil cup and empty and carefully wipe it. Throw away all oil samples after once using in making test. Pour cold water into the water bath, allowing it to overflow into the receptacle until the temperature of the water in the batch is lowered to 8° below the flash-point of the oil as shown by the previous test. With cold water of nearly constant temperature it will be found that a uniform amount will be required to reduce the temperature of the water-bath to the required point. Place the oil cup back in the bath and measure into it a 50 c.c. charge of fresh oil. Destroy any bubbles on the surface of the oil, put on the cover with its thermometer, put in the heating lamp, record time and temperature of oil and water, and proceed to repeat tests as described above. Introduce test flame for first time at a temperature 5° below the flash-point obtained on the previous test.

Precautions.—Be sure to record barometric pressure either from laboratory barometer or from nearest Weather Bureau station. Record temperature of room. Note and record any flickering of the test flame or slight preliminary flashes when the test flame is introduced into the cup before the proper flash occurs. Record time and temperature of such flickers or slight flashes, if they occur.

The Abel closed-cup tester in its improved form, the Abel-Pensky apparatus, has a water-bath and is adapted to oils having a moderately low flashing-point, such as kerosenes. The modified Pensky-Martin apparatus, as recommended by the U. S. Bureau of Mines, may be used successfully with almost any oil. It will be described under Lubricating and Fuel Oils.

Additional closed-cup testers are the New York State Board of Health or Elliott tester specified in some states.

Open cup testers will be described under Lubricating Oils and under Asphalts.

A typical comparison of flash-points as obtained by the use of different forms of apparatus shows:

A. S. T. M. closed tag	100° F.
Elliott or N. Y. closed	100°–105° F.
Abel	102°–106° F.
Abel-Pensky	102°–105° F.
Pensky-Martin	102°–106° F.
Tag, open cup	108°–112° F.
Clarland open cup	110°–115° F.

To correct readings made at other pressures other than barometric pressure of 760 mm.:

BAROMETER IN MILLIMETERS	CORRECTION, DEGREES C.
700	−2.1
705	−1.9
710	−1.7
715	−1.6
720	−1.4
725	−1.2
730	−1.0
735	−0.9
740	−0.7
745	−0.5
750	−0.3
755	−0.2
760	0
765	+0.2

COLOUR DETERMINATION OF REFINED PETROLEUM (KEROSENE, NAPHTHA, GASOLINE)

The Saybolt apparatus consists of two colour comparison tubes, one being arranged for insertion of a standard yellow glass in the bottom, the other being graduated for different lengths of oil column.

The yellow glass discs are supplied with each chromometer.

Two glasses are used to determine colour shades up to and including +15, and only one glass from +16 to +25

An excess of oil is filled into the graduated tube so that in drawing off the excess the colour of the oil becomes lighter.

The apparatus should be set at a window having a one-light sash, so that a good light is reflected from the mirror, but not in the direct rays of the sun, and care should be taken that no coloured light is reflected toward the instrument from surrounding buildings, tanks or other objects.

Clean the chromometer before making a new test, by allowing some of the oil to be tested to run through the graduated tube.

For the purpose of most easily determining colour shades, the colour of the column of oil when nearing the colour of the standard glass discs, is lowered shade by shade by use of the pet cock.

Now lower the column of oil one shade more and if it appears whiter than the standard glass disc, the colour of the oil is recorded one shade above this last whiter point.

It is evident that no oils are to be compared with one disc unless they positively show whiter at $10\frac{4}{8}$ in. with two discs.

Moreover, a full tube (20 in.) of white oil that shows whiter than one (1) disc must rate over +25.

ONE DISC

INCHES OF OIL IN TUBE	COLOUR SHADES	
20	+25	"Water-white"
18	+24	
16	+23	
14	+22	
12	+21	
$10\frac{6}{8}$	+20	
$9\frac{4}{8}$	+19	
$8\frac{2}{8}$	+18	
$7\frac{2}{8}$	+17	
$6\frac{2}{8}$	+16	

TWO DISCS

Inches of Oil in Tube	Colour Shades		Inches of Oil in Tube	Colour Shades	
$10\frac{4}{8}$	+15	Standard white	$5\frac{4}{8}$	+4	Standard white
$9\frac{6}{8}$	+14		$5\frac{2}{8}$	+3	
9	+13		5	+2	
$8\frac{2}{8}$	+12		$4\frac{6}{8}$	+1	
$7\frac{6}{8}$	+11		$4\frac{4}{8}$	0	
$7\frac{5}{8}$	+10		$4\frac{2}{8}$	−1	
$6\frac{6}{8}$	+ 9		4	−2	
$6\frac{4}{8}$	+ 8		$3\frac{6}{8}$	−3	
$6\frac{2}{8}$	+ 7		$3\frac{5}{8}$	−4	
6	+ 6		$3\frac{4}{8}$	−5	
$5\frac{6}{8}$	+ 5		$3\frac{3}{8}$	−6	
			$3\frac{2}{8}$	−7	
			$3\frac{1}{8}$	−8	
			3	−9	

Other chromometers that have been used in England and Germany are the Wilson and the Stammer instruments. The former uses standard colour glasses known as *good merchantable*, *standard white*, *prime white*, *superfine white* and "*water-white*" with which a uniform depth of oil is to be compared. The Stammer instrument measures a variable length of oil column comparing it with standard colour glasses and measuring the length of the oil column in millimeters.

Still another form of colour measuring instruments, the Lovibond tintometer uses an extensive series of coloured glasses.

In the absence of any instrument, standard acidified potassium dichromate solutions may be prepared to correspond with the colours of the Saybolt tubes. Each of these solutions when placed in 4 ounce sample bottles and marked with the equivalent Saybolt value may be used to match samples.

Saybolt Colour	Mgrm. of Potassium Dichromate per 100 c.c. of 1 % Sulphuric Acid Solution	Saybolt Colour	Mgrm of Potassium Dichromate per 100 c.c. of 1 % Sulphuric Acid Solution
25	0.20	9	1.95
24	0.30	8	2.05
23	0.37	7	2.17
22	0.45	6	2.30
21	0.55	5	2.40
20	0.65		
19	0.75	4	2.55
18	0.85	3	2.65
17	0.95	2	2.75
16	1.10	1	2.85
15	1.25	0	3.00
14	1.35		
13	1.50		
12	1.65		
11	1.75		
10	1.85		

Distillation test of kerosene. The apparatus (Engler flask) and procedure are essentially those already described under Gasoline with minor differences. The Bureau of Mines specifies in its application of this method to kerosene distillation that the hard asbestos board, 6 by 6 by 1/4 in., upon which the distillation bulb rests, shall have a hole 1 1/2 in. in diameter in its center and prescribes the high-distillation thermometer of the American Society for Testing Materials, which is filled with nitrogen and has a range of 0° to 400° C.

Burning quality tests are more for the refinery laboratory than for the consumer and are not generally included in the tests asked of the commercial analyst. However, the U. S. Bureau of Mines gives in its list of recommended methods two lamp burning tests for ordinary kerosene and special tests for long time burning oil, for mineral seal oil and for signal oil.

The estimation of sulphur in kerosene is a matter of some importance, as sulphur impurity in an oil tends to cause carbonisation of the wick and to evolve disagreeable odours in burning. The amount of sulphur in a good illuminating oil should not exceed 0.06%, but many lower grades may contain 0.10% or more.

The method of the American Society for Testing Materials, as given by the Bureau of Mines in their "Methods for Testing Petroleum Products," is as follows:

The apparatus required includes an absorber of chemically resistant glass, about 150 c.c. capacity, containing glass beads or short pieces of glass rod in the suction side.

Chimney of chemically resistant glass connected with the absorber by a rubber stopper.

Spray trap of chemically resistant glass connected with the absorber by a rubber stopper.

Small lamp of about 25 c.c. capacity. This lamp may conveniently consist of a 25 to 35 c.c. Erlenmeyer flask and a cork carrying a short section of glass tubing about 1/8 in. in inside diameter. The cork must be grooved along the sides, so that air may enter the flask while the oil is being consumed.

Ordinary cotton wicking.

Filter pump or other means for continuous suction and rubber tubing to connect with spray trap.

The solutions required are:

Hydrochloric Acid.—Solution containing 2.275 grm. HCl per litre, carefully checked for accuracy.

Sodium Carbonate.—Solution containing 3.306 grm. Na_2CO_3 per litre. Exactly 10.0 c.c. should be required to neutralise 10.0 c.c. of the hydrochloric acid solution.

Methyl Orange.—Solution in distilled water, containing 0.004 grm. Methyl Orange per litre.

Pass two strands of new cotton wicking, about 4.5 in. long, through the ⅛-in. diameter wick tube so that they are not twisted but parallel in the wick tube. Trim the wick with very sharp scissors. Pour into the clean, dry lamp about 20 c.c. of the oil to be tested, insert the wick, and cork and weigh the assembly with an accuracy of 0.001 grm. It is advisable to make a blank estimation at the same time and under the same conditions by burning sulphur-free alcohol in a similar lamp.

Rinse the absorber containing the glass beads thoroughly with distilled water and add exactly 10.0 c.c. of the standard sodium carbonate solution from an accurately calibrated burette, allowing the burette to drain for 3 minutes before the reading is taken. Rinse the chimney and the spray trap with distilled water, dry the chimney, and connect both with the absorber. Set up the apparatus for the blank determination in exactly the same manner, using exactly 10.0 c.c. of the sodium carbonate solution. Apply gentle suction to both absorbers, light both the weighed oil lamp and alcohol lamp, and then place in position under the chimneys, so that the tops of the wick tubes extend into the chimneys not more than 1/16 in. Adjust the wick height and the suction so that the flame is steady, free from smoke, and approximately ¼ in. high. This requires that the wick be flush with the top of the wick tube for naphthas and a little higher for illuminating oils. The room must be free from draughts. The suction on the blank should be so adjusted that air is drawn through both lamps at the same rate. Continue burning for about 2 hours, or less if the sulphur content of the oil is high. During this time the oil should be consumed at the rate of about 1 grm. per hour.

Extinguish the flames and stop the suction on both absorbers. Weigh the oil lamp immediately and calculate by difference the weight of oil consumed. Working with the blank first, disconnect the spray trap and chimney and wash them thoroughly with the methyl orange solution, using a wash bottle with a very fine jet and collecting the washings in the absorber. The amount of solution required for washing should not exceed 35 c.c. Carefully titrate the very faintly yellowish solution in the absorber with standard HCl, added to the suction side of the absorber from an accurately calibrated burette. During this titration the contents of the absorber should be agitated carefully, either by blowing through a rubber tube held between the operator's lips and connected at the other end with the chimney side of the absorber, or else by the use of a suitable rubber syringe bulb. As the end point is approached, draw the liquid back into the chimney side between each addition of acid and then blow it into the suction side, agitating as before. As soon as the first permanent pink colour appears the end-point has been reached. Read and record the volume of HCl solution used.

Rinse the chimney and spray trap used in the actual estimation into the absorber with which they were connected, exactly as prescribed for the blank. If the methyl orange solution in the absorber has a pink colour, too much oil has been burned and the estimation must be repeated, burning for a shorter time. Titrate just as in the blank, making sure that the absorber is cold. Read and record the volume of HCl solution required.

Calculate the sulphur content of the oil by substituting the proper values in the following formula:

Percentage of sulphur

$$= \frac{(\text{HCl for blank, c.c.} - \text{HCl for sample, c.c.}) \times 0.1}{\text{grams of oil burned}}.$$

If blank is not run, the formula is:

$$\text{Percentage of sulphur} = \frac{(\text{Na}_2\text{CO}_3\text{, c.c.} - \text{HCl, c.c.}) \times 0.1}{\text{grams of oil burned}}.$$

These formulas are correct only for the standard solutions specified, 1 c.c. of each being equivalent to 0.001 grm. of sulphur. The use of solutions of other strength, such as N/10, involves more complicated calculation and is not advisable.

Conradson (*J. Ind. Eng. Chem.*, 1912, 4, 842) has modified the lamp-burning test for sulphur so as to differentiate between the sulphur compounds that might be present in the oils and to allow of the application of the test to the testing of lubricating oils as well as kerosene. He burns a larger amount of oil in the lamps and also consumes all the oil in the oil fount, as well as makes a careful examination of the sulphur compounds that may remain in the wick from the oil. This process will be referred to under lubricating oils.

The **"doctor" test** to determine whether a sample is "sweet" or "sour" is applied to kerosenes as well as to gasoline. It has been already described under gasoline testing methods.

The **"floc" test** for kerosene is made by taking a 500 c.c. Florence or Erlenmeyer flask, into which is put 300 c.c. of the oil (after filtering if it contains suspended matter) and suspending a thermometer in the oil by means of a cork slotted on the side. The flask is then placed on a sand bath, which is heated so that the oil reaches a temperature of 240° F. at the end of 1 hour. The oil is held at a temperature of not less than 240° F. nor more than 250° F. for 6 hours. The oil may become discoloured but there should be no suspended matter formed in the oil. The flask should be given a slight rotatory motion and if there is a trace of "floc," it can be seen to rise from the centre of the bottom of the flask.

KEROSENE EMULSIONS

So-called kerosene emulsions used for spraying fruit trees, etc., are mixtures of soap, kerosene and a little water. In addition to kerosene, there may be tar acids combined as soaps and aromatic hydrocarbons. Crude petroleum may be used instead of kerosene.

The emulsion may be broken and the oil extracted by drying, but that means loss of light constituents of the oil. S. S. Sadtler (*J. Ind. Eng. Chem.* 1909, **1**, 479) suggests that the best way, probably, is to add enough alcohol to a measured portion for analysis to break the emulsion completely and then add two or three times as much ether as alcohol and proceed as given on page 137.

The soaps generally contain rosin as well as fatty constituents. The soaps from these mixtures are examined after the removal of the oils, as just referred to, and any separation of different kinds of oils is effected after driving off the ether. Benzene homologues can be separated from petroleum oils by means of concentrated nitric acid, which converts the former into nitro-derivatives.

Water is estimated in kerosene emulsion by means of distillation from a retort, the one frequently used being a cylindrical copper retort holding about 1 litre, obtained from The Barrett Co., U. S. A.

The burner is ring-shaped and surrounds the retort. With many oils, water causes frothing, so it has been found best to start the heating with the burner at about the upper level of the liquid and then lower it after danger of frothing is over. A little petroleum benzine (62° Bé.) may be added in cases where the hydrocarbons are of high b. p. so as to carry over the water.

GAS OIL

The petroleum oils used for gas-making are usually those yielding only small percentages of kerosene, although any grade of crude oil may be used, but in any case, they are distilled to the exclusion of nearly all other products. The main product is a single cut of gas oil.

Owing to the rapid increase in the use of gas oil for gas-making, the importance of selecting the most suitable grades of crude oil has been recognised, and it has become necessary to devise analytical tests for this purpose. The valuation of an oil is determined by the following tests which are arranged in alphabetical order.

Asphalt
Bromine number
Calorific value
Cold test
Cracking test
Distillation
Flash-point
Fire-point
Paraffin
Sediment
Specific gravity
Sulphur
Water

All tests are not necessary for general routine analysis. The most important and most commonly used tests are cracking test, cold test, distillation, flash-point, fire-point, sp. gr., sulphur, and water tests. Of these, the cracking test is of most value in obtaining the valuation of an oil for gas-making.

Sampling of Gas Oil.—The sampling of gas oil is of primary importance, and every effort should be made to procure a representative sample of the lot to be tested. As the analyst is familiar with the various methods and devices for sampling liquids, this subject requires no further discussion.

Asphalt.

(See page 90.)

As the asphalt content is in approximate relation to the coke, this test is an indication of the quantity of residue expected on distillation of gas oil.

Bromine Number.—(See page 195.)

Calorific Value.—(See page 85) Sherman and Kropff (*J. Amer. Chem. Soc.*, 1918 **30**, 1626–31) found that fairly exact relations existed between the sp. gr. of petroleum oils and their calorific value. 64 samples of typical American petroleum oils from the chief oil fields, and ranging from light gasoline to heavy crude oil, were examined. The relationship is expressed in B.t.u. per pound, and compared with the density, expressed in degrees Baumé. The following formula expresses the relationship approximately:

$$\text{B.t.u.} = 18{,}650 + 40\ (\text{Baumé degrees} - 10).$$

In the case of 90% of the samples examined the differences between the observed and calculated calorific values were less than 1%; it was greater than 2% in 1/30 of the cases, and in no case was greater than 3%. Only 2 of 63 samples showed a difference of as much as 100 calories, and 7 of as much as 50 calories, between the observed and calculated powers.

Cold Test.—This test (A. H. Gill, Oil Analysis) may be defined as the temperature at which oil will just flow.

A 4-oz. glass vial is one-fourth filled with the oil to be examined, a short, rather heavy thermometer inserted in it, and the whole placed in a freezing mixture. When the oil has become solid throughout, the vial is removed, the oil allowed to soften, and thoroughly stirred until it will run from one end of the vial to the other. The reading of the thermometer is now taken and recorded.

Freezing mixtures may be made from ice and water, or from ice and salt, when temperatures as low as −30° F. are procurable.

This test is conducted and the necessary precautions are observed, to facilitate the mechanical handling of gas oil in localities and seasons, when low atmospheric temperatures are likely to be experienced.

Cracking Test.[1]

The chief test to be applied is that of using a small retort to determine the amount of gas obtainable and its candle-power, as well as the yield of tar. J. F. Tocher (*J. Soc. Chem. Ind.*, 1894, **13**, 231) described a cylindrical iron retort, 36 by 6 in., and in a series of tables

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[1] Another method for the cracking test and one which is devised more especially for gas oil laboratories may be found in Gas Chemists, Handbook, 2nd ed., 1922, p. 66.

TABLE I.—PRODUCTS YIELDED BY VARIOUS OILS

Temperature	Mineral naphtha sp. gr. 0.730		Burning oil sp. gr. 0.807		Mineral oil sp. gr. 0.847			Mineral oil sp. gr. 0.884		
	600°	850°	600°	850°	600°	800°	1100°	500°	600°	850°
Cubic feet per gallon of oil	72	100	75	93	64	82	95	34	59	108
Colour of gas	White	White	White	Brownish-white	White	Light brown	Dark brown	Light yellow	Light yellow	Brown
Composition of gas	%	%	%	%	%	%	%	%	%	%
C_nH_n hydrocarbons	31.2	29.8	32.8	43.1	33.7	46.2	21.5	44.7	40.5	35.7
C_nH_{2n+2} hydrocarbons	47.6	48.7	57.0	47.2	50.1	39.4	49.2	40.1	48.2	46.3
Hydrogen	17.4	19.1	7.1	7.6	13.7	11.9	28.4	12.7	8.1	16.1
Carbon density of C_nH_n	2.67	2.71	3.93	2.92	2.88	2 [illegible]	2.41	3.11	2.95	2.79
Hydrogen density	......	......	......	......	4.87	5.22	5.16	5.38	5.54	4.46
Illuminating power. In candles corrected to 5 cu. ft. of gas and 120 grains sperm per hour	43.5	42.2	48.7	61.4	52.5	64.8	36.2	63.8	57.7	49.0
Candles per gallon	626	844	730	1142	672	1062	688	434	681	1058
Pounds sperm per candle	3292	4437	3482	5447	3046	4815	3119	1885	2958	4596
Enriching value, pounds sperm	......	......	......	6 % mixture gave 10,174 enrichment figure = 118.	......	5 % mixture gave 6,872; enrichment figure = 96.5	......	......	......	......
% Residuals %	11.4	5.1	21.4	7.5	28.5	12.2	18	62.3	41.5	9.4

TABLE II.—PRODUCTS YIELDED BY VARIOUS HYDROCARBONS

Temperature	Octane, C_8H_{18}; b. p. 122°		Decane, $C_{10}H_{22}$; b. p. 156.5°		Turpentine oil, $C_{10}H_{16}$; b. p. 154°–158°	Naphtha, sp. gr. 0.730	Mineral oil, sp.gr. 0.884	
	550°	800°	550°	800°	800°	850°	500°	850°
Yield	18 litres per 100 c.c.	42 litres per 100 c.c.	24.6 litres per 100 c.c.	47.5 litres per 100 c.c.	63.3 cubic feet per gal.	100 cubic feet per gal.	34 cubic feet per gal.	0.108 cubic feet per gal.
Colour of gas	White	White	White	White	White	White	Light yellow	Brown
Composition of gas.								
C_nH_n hydrocarbons	23.5	12.3	27.4	13.4	19.1	29.8	44.7	35.7
C_nH_{2n+2} hydrocarbons	39.4	35.4	36.0	50.1	54.1	48.7	40.1	46.3
Hydrogen	35.7	52.8	35.7	36.5	26.8	19.1	12.7	16.1
Ethylene equivalent of C_mH_m	30.0	11.7	32.1	14.2	30.4	35.2	69.5	49.8
Carbon density	2.56	1.91	2.35	2.12	3.20	2.71	3.11	2.79
Illuminating power in candles per 5 cubic feet	18.0	....	20.2	12.0	39.1	42.2	63.8	49.0
Residuals, %	22.0	a few drops	50.0 Composed almost entirely of unchanged decane	none	16.6	5.1	62.3	9.4

showed the nature of the products (1) from various oils; (2) from various hydrocarbons; and (3) the character of mixtures of oil-gas and coal-gas in various proportions. Although there have been better constructed retorts introduced for laboratory tests more recently, the results of Tocher are of considerable value.

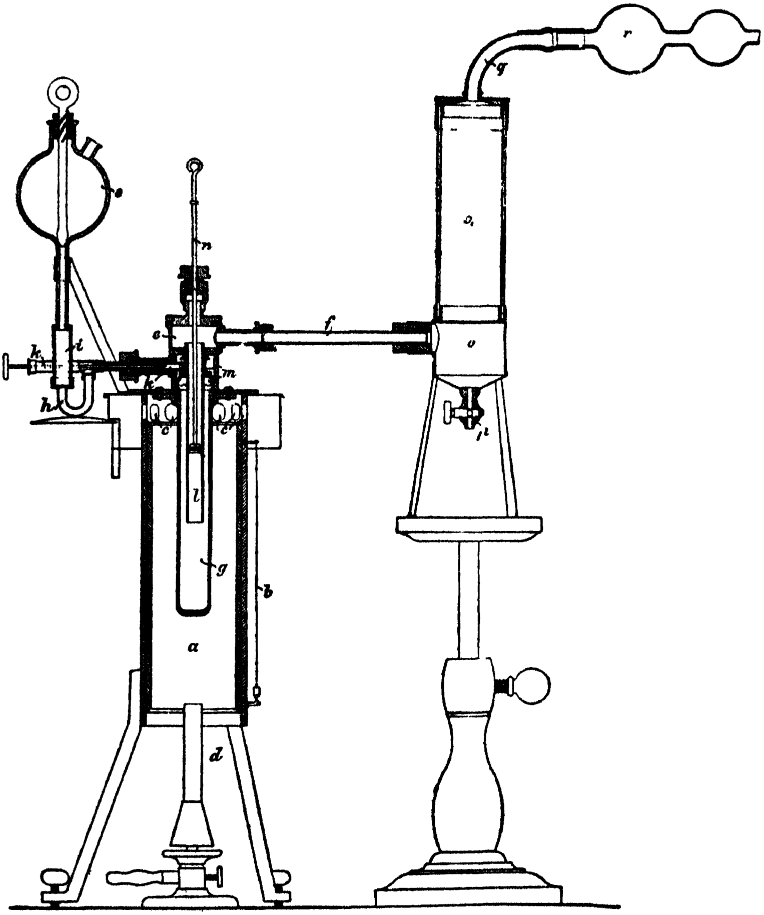

Fig. 11.

The most practical laboratory retort for determining the gas value of an oil that has been devised is that of Helfers (*Z. angew. Chem.*, 1896, 451). Fig. 11 shows the retort and connections. 100 c.c. of oil are placed in the Hofmann funnel *s* and go through the glass cylinder *i* and the U-tube *h* to the needle valve *k*, where it is admitted a drop at a time into the retort *g*. The passages *s*, *h* and *k* are weighed before and after the test to get the exact weight of oil taken, and the retort *g* for the amount of coke and oil for tar. The oil is introduced at the rate of 10–30 drops per minute after the retort has been brought up to red heat. If the delivery tube becomes clogged with tar, the piston *n* is used to force a passage. When the gas-making is normal the gas has a brown colour and the tar is dark coloured; if the gas is white and the tar clear brown, there has been an incomplete gassification.

The candle-power of the gas, on an average gas yield of 50 c.m. from 100 kg. of oil, is calculated according to the following formula:

A = gas yield, C = amount of coke, T = the amount of tar and L = photometric value of the gas, $L_{50} = \frac{L(A - 50)(CT)}{100}$ in regular gas ovens.

The conditions of an experiment carried out by F. Frank (Holde, Untersuch. d. Mineralöle u. Fette, p. 64) were as follows:

Temperature of the upper retort	limits	670°–690°
	average	680°
Temperature of the lower retort	limits	740–750°
	average	745°
Time of experiment		40 minutes
Amount of oil gassified		12.91 kg.
Resulting gas in cubic metres		7.70 m³.
Resulting tar		4.45 grm.
Gas oil used for one run		19.37 kg.
Gas yield for one run		11.55 m³.
From 100 kg. of oil there was obtained:		
Gas in m³		59.64
Gas in kg		34.47
The gas burning at the rate of 35 litres per hour in burner No. 60 gave the following in Hefner candles		11.3

Distillation.[1]—(See page 83.)

Flash- and Fire-point.—The flash-point of an oil is the temperature to which the oil must be heated to give off vapours which, when mixed with air, produce an explosive mixture. The fire-point is the lowest temperature to which an oil must be heated to give off vapours which, when ignited, will burn continuously.

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[1] A more detailed method than the above which applies more particularly to gas oil is to be found in A.S.T.M., 1923, 23, p. 703.

(For the details of test see page 136. Also, Gas Chemists' Handbook, Second Edition, 1922, p. 77.)

Paraffin.—(See page 90.)

Sediment.—Treat a 5 grm. sample of the oil under examination with a large excess of petroleum spirit and filter the whole through a tared Gooch crucible. Wash the sediment in Gooch crucible several times with petroleum spirit until the washings show no discoloration. Heat the crucible for two hours at 105°, desiccate, and weigh. The difference in weight of the crucible will be the quantity of sediment.

Specific Gravity.—The specific gravity is taken in a pycnometer at 25°, and referred to water at the same temperature. Where great accuracy is not required a hydrometer may be used for this test.

Sulphur.—(See page 85.)

Water.—(See page 81 or A.S.T.M., 1923, **23**, p. 694.)

U. S. Specifications for Burning Oil (1921). "Water-white" Kerosene

General.

1. This specification covers the grade of kerosene used by the United States Government and its agencies as an illuminating oil. This oil may be used as fuel and for cleaning in case of necessity.

2. The oil shall be free from water, glue and suspended matter.

Properties and Tests.

3. Colour: the colour shall not be darker than No. 21 Saybolt.

4. Flash-point: the flash-point shall not be lower than 150° F. (closed tester-tag).

5. Sulphur: the sulphur shall not be more than 0.06%.

6. Floc: the "floc" test shall be negative.

7. Distillation: the end-point shall not be higher than 600° F.

8. Cloud test: the oil shall not show a cloud at 0° F.

9. Doctor test: the "doctor" test shall be negative.

10. Burning test: the oil shall burn freely and steadily for 18 hours.

All tests shall be made according to the methods for testing burning oils adopted by the Committee on Standardisation of Petroleum Specifications.

Long Time Burning Oil

Oil for use by the Bureau of Lighthouses shall be as described as the Department of Commerce, which specifications, etc., at the present time are as follows:

1. The kerosene must have a flash-point of not less than 140° F. and fire-point of not less than 160° F. (tag closed tester).

2. The kerosene must contain no free acids or mineral salts. Litmus paper immersed in it for five hours must remain unchanged.

3. One hundred grm. of kerosene shaken with 40 grm. of sulphuric acid (sp. gr. 1.73) must show little or no coloration.

4. When distilled from a still so jacketed as not to allow of local heating at a rate of not over 10% in 10 minutes, the kerosene shall not distil below 350° F. and 98% shall distil under 515° F., the temperature taken being that of the condensing vapour.

5. When burned for 120 hours in a lens lantern supplied with a fifth order oil lamp, the kerosene must burn steadily and clearly without smoking, with minimum incrustation of wick, slight discoloration of chimney and less than 10% loss of candle-power. A lamp of this description will be loaned to successful bidder.

LUBRICATING OILS

Lubrication has for its object the reduction of friction between moving surfaces. In the sliding friction of solids the magnitude of the resistance is, up to the point of abrasion, dependent on the character of the surfaces, and proportional to the force with which they are pressed together, though, when the pressure is very low, the resistance may be principally due to adhesion, in the case of very smooth or polished surfaces. By the introduction of a suitable third medium between the frictional surfaces, which medium may be solid (such as graphite, talc, white lead and the like) or of an oily nature (such as lubricating grease or lubricating oils), the **solid** friction may be partially or wholly eliminated, and with the latter mentioned media, replaced with "soft solid" or fluid friction. Roller bearings and ball bearings are excepted in this connection. In **fluid** friction, the resistance is proportional to the area and velocity of the surface exhibiting it, and to the density and viscosity of the liquid. In the practical application of lubricants to the rubbing surfaces of machinery in motion, the friction is usually compounded of the friction of solids and of fluids in proportions varying in each case. In cases, however, in which it is practical to float the moving part in the lubricant, fluid friction alone is concerned; while in the case of slowly moving heavy machinery, the resistance is chiefly due to the friction of solids.

In theoretically perfect lubrication the resistance would be independent of the pressure. The more viscous the lubricant, the greater the pressure which can be sustained without squeezing out the film of lubricant from between the moving surfaces; but *unnecessarily* high viscosity creates unnecessary fluid friction, and the viscosity of the lubricant should therefore be proportional to the pressure. In other words, the lubricant should have just sufficient "body" or viscosity to keep the moving surfaces apart, under the maximum pressure. Hence for heavy machinery a highly viscous or even solid lubricant must be employed, and oils are not unfrequently wholly or partially replaced by graphite, steatite, wood saturated with waxes, etc. (so-called oilless bearings).

A combination of this kind is Acheson's "oil-dag" or lubricating oil in which is suspended deflocculated graphite, or graphite which has been brought to a very finely divided state by a process invented by E. G. Acheson, of Niagara Falls, N. Y. For delicate movements such as exist in clocks and watches a light and fast-running machinery, the thinnest oils are suitable.

A thick oil takes a greater power to drive, and develops a higher temperature than an oil of low viscosity; and, as a rule, the lubricant should be as thin as is consistent with the weight of the machinery and the temperature to which the oil will be subjected. With ample driving power a moderately thick oil may be used for heavy machinery, particularly if the temperature be high, but if the driving power be inadequate, it may be necessary to use a thinner oil.

Although the foregoing is the main principle governing the choice of lubricants, the degree of viscosity required is also dependent on the fit of the bearing surfaces and upon the character of the motion, and these conditions vary largely in each case. It is very difficult to predict the behaviour of a particular oil in practice from its trial in a mechanical testing machine. On this account, as also from the more efficient of them necessitating the use of steam-power, the ingenious machines devised for testing lubricating oils have not fully justified the anticipations of their inventors. The only rational plan of applying such tests is to use a series of standard spindles for testing spindle oils, standard bearings for axle-lubricants, and so on for other oils. This requirement is practically prohibitory of the use of mechanical testers in an ordinary laboratory, and it is fortunate that a close relationship exists between the viscosity of an oil and its characters as a lubricant. In other words, if a given oil is satisfactory under known conditions of fit, pressure, speed, and temperature, it may be predicted with tolerable certainty that another oil of the same nature, having a similar viscosity, will yield equally good results.

The one serious drawback in this deduction is that it only holds true with oils from the same, or similar, crudes. The tests of an oil made from Texas crude may be exactly the same as those made from a Franklin (Pa.) crude, but they will not do the same work. The nature of the hydrocarbons plays a most important part in the matter. For the foregoing reason it is impossible for a chemist to certainly predict the action of an oil from his tests unless he knows the stock from which it was made.

The characters which should be taken into consideration in forming an opinion on the suitability of a lubricating oil for a particular class of work are:

1. The viscosity or "body" of the oil at the temperature at which it is to be used.
2. The temperature at which the oil thickens or actually solidifies.
3. The flash-point, or temperature at which the oil gives off inflammable vapour in notable quantity.
4. The volatility, or loss in weight which the oil suffers on exposure in a thin film to an elevated temperature.
5. The "gumming" character, or tendency of the oil to become oxidised.
6. The proportion in which the fatty and hydrocarbon oils of a mixture are present.
7. The proportion and nature of the free acid, if any, in the oil.
8. The tendency of the oil to act on metals.
9. The presence of mineral matters, such as the bases of soaps.
10. The presence of graphite.
11. The presence of tarry matter.
12. The presence of metal particles in a recovered (filtered) oil.

C. F. Mabery and J. H. Williams (*J. Amer. Chem. Soc.*, 1908, **30**, 992–1000) have determined the relative lubricating values of corresponding members of the different series of hydrocarbons found in petroleum. The following tables show some of the results obtained by Mabery and Williams. The hydrocarbon series having the least hydrogen were found to have the greatest viscosity and lubricating value. This had been known in a general way from practical experience. For instance, it had been known for some time that the viscosity of melted paraffin was much less than hydrocarbons of the same b. p. of series lower in hydrogen. This work of the above-mentioned authors is quite detailed in its proof and is of great commercial importance. Table A shows comparisons of sp. viscosity in two cases between higher and lower series, and table B similar results, with actual friction tests in addition.

TABLE A (60°)

Series	B. p.	Sp. gr.	Sp. vis.
C_nH_{2n+2}	294–296° (50 mm.)	0.781	10.88
C_nH_{2n-2}	294–296° (50 mm.)	0.841	21.23
C_nH_{2n+2}	274–276° (50 mm.)	0.775	8.51
C_nH_{2n}	274–276° (50 mm.)	0.835	15.63

The coefficient of friction $C = F/P$ frictional resistance F, divided by total pressure between rubbing surfaces PU at the beginning of a test, will be the sum of the *kinetic* friction, applying to surfaces in motion, and the *static* friction developed when the two surfaces begin their movement one against the other. This latter may be very considerable if the pressure when the two surfaces were at rest had squeezed out the film of lubricants, and a new film must be developed as motion continues. "The high values for the static coefficient of friction explain the great effort often required to start engines or machinery from rest and form one of the chief reasons why ball and roller bearings are used, as with surfaces in rolling contact there is practically no difference between the static and the kinetic coefficient of friction" (*Thomsen*, *Practice of Lubrication*, 1920, p. 83).

Viscosimetry.—As already stated, the viscosity or "body" of an oil is the most important criterion of its suitability as a lubricant under certain conditions, and hence great interest is attached to its satisfac-

TABLE B.—COMPARATIVE LUBRICATING VALUES OF HYDROCARBON SERIES

Oil treated	B. p.	Sp. gr.	Sp. vis. 20°	Test of durability, mins.	Temp.			Coef. of friction		
					Start	2 hrs.	Break	Start	2 hrs.	Break
Hydrocarbon C_nH_{2n}	274–276° (50 mm.)	0 861	37.57	120	76°	107°	124°	0 02	0.01	0 015
Hydrocarbon C_nH_{2n-2}	312–314° (50 mm.)	0.868	88.16	150	80°	130°	185°	0 01	0 02	0.02
Hydrocarbon C_nH_{2n-x}	228–230° (30 mm.)	0 923	94.3 Viscosity	210	75°	113°	164°	0 03	0 01	0 01
Castor		0 97	104 (210°)	150	70°	165°	225°	0 04	0 025	0.03
Sperm		0.94	192 (90°)	140	70°	120°	160°	0 02	0 01	0.01
Rape		0.91	108 (150°)	120	80°	160°	230°	0.03	0 02	0.05
Cylinder oil (comp.)		0.92	123 (212°)	75	80°	180°	210°	0 05	0 03	0.06
Cylinder oil (comp.)		0 89	135 (210°)	200	80°	185°	225°	0.07	0 03	0.06

tory determination. It has acquired greater importance of late years, owing to the rapidly increasing employment of mineral lubricating oils as substitutes for the fatty oils formerly used. Thus, different specimens of any given fixed oil, such as sperm oil or rape oil, vary in viscosity only within comparatively narrow limits at a given temperature, and hence an engineer accustomed to use a given fixed oil would, in purchasing such oil, derive little advantage from a knowledge of the viscosity of a particular sample of such oil. On the other hand, mineral lubricating oils may be manufactured of any required viscosity within comparatively wide limits, and hence it is very important that an engineer should be able to ascertain whether further supplies of this class of lubricant are of a viscosity similar to that of the oil previously employed.

It was formerly assumed that the viscosity of an oil bears a tolerably definite relation to its sp. gr., but the fact that this is an error is now generally recognised.

Temperature has much influence on the viscosity of oils, and is greatest in those which are solid, or partly so, at ordinary temperatures. The thicker animal oils, containing much stearine, are most sensitive to an increase of temperature. Many mineral oils, however, though fluid at ordinary temperatures, decrease in viscosity so rapidly when heated as to have quite different characters at high temperatures. This fact must be kept in mind when an oil is to be used in an engine cylinder or under similar conditions. As the temperature of a given friction surface is liable to vary considerably, preference should be given to an oil which shows the least variation in viscosity, with the limits of temperature to which it is likely to be subjected.

Boverton Redwood (*J. Soc. Chem. Ind.*, 1886, 5, 128) has determined by his standard viscosimeter (page 129) the comparative rates of flow of a number of oils for every rise of 10° F. The following figures are the number of seconds required for 50 c.c. of each oil to flow through an orifice out of which an equal measure of water at 60° F. ran in 25.5 seconds:

On examining the results recorded in the foregoing table, it will be observed that sperm oil is remarkable for the comparatively slight reduction in its viscosity caused by increase of temperature, a property to which the value of this oil as a lubricant for use under very varied conditions is probably due. The Russian mineral oils lose their viscosity with an increase of temperature more rapidly than American oils of the same sp. gr., but in both classes the reduction is most rapid in the case of the most viscous oils, and, as the Russian oils have a higher viscosity than the American, a more rapid reduction in the former case might be anticipated.

Temperature; °F.	Refined rape oil	Beef tallow	Sperm oil	Neatsfoot oil	American mineral oil, sp. gr. = 0.885	American mineral oil, sp. gr. = 0.913	American mineral oil, sp. gr. = 0.923	Russian mineral oil, sp. gr. = 0.909	Russian mineral oil, sp. gr. = 0.915	Russian mineral oil, semi-solid
50	712·5	......	......	620	145	425	1030	2040	2520	......
60	540	......	177	470	105	295·5	680	1235	1980	......
70	405	......	137	366	90	225	485	820	1320	......
80	326	......	113	280	73	171	375	580	900	......
90	260	......	96	219	63·5	136	262	426	640	......
100	213·5	......	80·5	175	54	111	200	315	440	1015
110	169	......	70·5	147·5	50	89·5	153	226	335	739·5
120	147	......	60·5	126	47	78	126	174	245	531
130	123·5	......	57	112	44·75	63·5	101	135·5	185	398·5
140	105·5	......	51	88·5	41	58	82	116	145	317·5
150	95·5	......	49	75·5	37·5	52	70·5	95	115	250
160	85	......	47·5	70	......	46	63·5	83·5	93·5	200
170	76	......	46	62	......	......	58	70·5	77·5	161
180	69	......	44·5	56·5	......	......	52·5	61·5	67·5	134·5
190	64·5	......	43	53	......	......	47	56·5	61	115·5
200	58·5	54·5	42	50·5	......	......	42	48	54	99
210	54	......	41	48·5	......	......	40	......	......	85
220	54	......	39	47	......	......	38	......	......	77
230	47·5	......	37	46	......	......	......	......	......	70·5
240	45·5	......	36	44·5	......	......	......	......	......	64·5
250	43·5	40	35	44	......	......	......	......	......	59
260	Viscosity slightly above the average	......	34	43·5	......	......	......	......	......	54
270		......	33	43	......	......	......	......	......	48·5
280		......	32	41·5	......	......	......	......	......	46·5
290		......	31	41	......	......	......	......	......	46
300		......	30	38	......	......	......	......	......	42·5

Oiliness.—The property in a lubricant, which causes it to adhere to metallic surfaces, appears to bear no direct relation to the physical properties of an oil; although it is greater for heavy viscosity oils than for low viscosity oils of the same character, yet two oils may have the same viscosity and the oiliness be much greater in the one than in the other. It is common knowledge that all fixed oils (vegetable and animal oils), or mixtures of mineral oils and fixed oils, possess greater oiliness than straight mineral oils. Thomsen states (*Practice of Lubrication*, 1920, 67) that a mixture of low viscosity distilled mineral lubricating oil and filtered cylinder stock has greater oiliness than a distilled mineral lubricating oil of the same viscosity as the mixture. Thomsen believes that this fact may perhaps be explained by the assumption that "the molecules of the fatty oil or cylinder stock adhere to the metallic surfaces in preference to the molecules of the distilled mineral oils; such coating of the surfaces with strongly adhering molecules would explain why it is possible with such blended oils to sustain almost as great pressures as if the fixed oil or filtered cylinder stock were used alone."

Wilson and Bernard (*J. Ind. Eng. Chem.*, 1922, **14**, 687) summarise their conclusions from a study of this oiliness quality as follows: animal and vegetable oils show consistently lower coefficients than ordinary refined mineral oils. The addition of very small amounts of fatty acids and of considerably larger amounts of neutral vegetable oils to mineral oils produces a very marked lowering of the coefficient of friction, thus confirming the statements of Southcombe and Wells. On metal surfaces, the maximum differences in the coefficients of friction for different oils are found in the neighborhood of zero velocity. In other words, the *static* coefficient of friction would appear to be the best single measure of the oiliness factor of a lubricant, especially considering the greater simplicity of the measurements. All of the above data confirm the belief that the oiliness factor of lubricants is due to a tenaciously adsorbed film of some constituent of the lubricant, the presence of which diminishes or prevents metal to metal contact, even after the surfaces have been pressed together for some time. This ability of the film to stand prolonged pressure without being squeezed out indicates that it partakes of the nature of a plastic solid with a fairly high yield point, rather than being a fluid film such as does the lubricating oil in a rapidly rotating bearing. In order to account for its remarkable effectiveness, even on surfaces with very appreciable irregularities, this film would apparently have to be much thicker than the mere monomolecular film which is frequently postulated on the difficulties of using a journal friction testing machine for measuring "oiliness," see article by Winslow H. Herschel of the U. S. Bur. Stan. (*Chem. Met. Eng.*, 1923, **28**, 594).

EXAMINATION OF LUBRICATING OILS AND GREASES

The *sp. gr.* of lubricating oils may be taken with greatest accuracy with a calibrated pycnometer, as mentioned in a previous section under Analysis of Gasoline, etc., but is usually determined in practice with a hydrometer graduated for the Beaumé scale. The correction for temperature is taken from the tables prepared by the U. S. Bureau of Standards.

The *colour* of lubricating oils may be observed with the Saybolt chromometer in the case of light coloured lubricating oils, but in most cases some form of tintometer is more useful. The Lovibond instrument, already referred to under illuminating oils, may be used or the modification of the tintometer adopted by the National Petroleum Association under the name of the Union Colorimeter. In this instrument the colour is determined by placing a 4-ounce bottle of the oil under examination in the right hand circular compartment. In the compartment behind the slot a 4-ounce bottle of water-white gasoline or distilled water is placed. Then place one of the standard glasses in the slot and close the slide. The instrument should than be directed toward a window so that the observer can compare the colour of the oil with the standard glass. Dark cylinder stocks, however, are usually examined by the iodine method, before mentioned under illuminating oils.

(For a table showing the values of the National Petroleum Association Standard grades in equivalents of the Lovibond colour scales and the iodine colour method see Kansas City Testing Laboratory, *Bul.* **16,** 442.)

Viscosity Determinations.—Reference has already been made to the views generally held as to the importance of a knowledge of how oils differ in this quality. The method generally accepted, in some form, by chemists is that of Poiseuille. He measures the rate of flow of the oil through a capillary tube, or a very narrow tube, under known conditions of temperature and pressure. We must for the sake of clarity distinguish between what is termed *absolute viscosity, kinematic viscosity,* as measured by the commercial viscosimeters, like the Saybolt, Redwood or Engler instruments, and *specific viscosity,* or ratio of the kinematic viscosity of the oil to that of water taken under the same conditions.

The absolute viscosity, as an expression of force, is expressed in dynes-second sq. cm. The term "*poise*" has been coined from the name Poiseulle and signifies "one dyne-second per sq. cm." The term "*Centipoise*" is used to represent one hundredth of a poise, just as one centimeter represents one hundredth of a meter. (A form of apparatus for the determination of absolute viscosity is described and illustrated by Eugene C. Bingham (*J. Ind. Eng. Chem.*, 1914, **6**, 233, and is now obtainable from the manufacturers Eimer and Amend, New York.)

Viscosity, as usually stated, is kinematic viscosity and is measured by any one of several instruments such as the Saybolt Universal viscosimeter, the Redwood viscosimeter or the Engler viscosimeter.

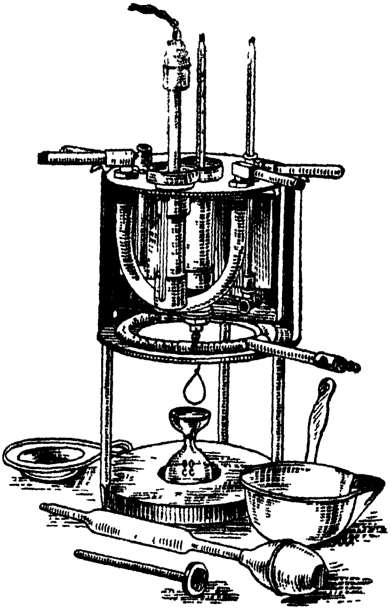

FIG. 12—Saybolt viscosimeter.

The *Saybolt Universal* is much used in the United States and is the instrument adopted by the American Society for Testing Materials, and the U. S. Bureau of Mines in its official "Methods for Testing Petroleum Products." The instrument is shown in Fig. 12.

The Saybolt viscosimeter is made entirely of metal. The standard oil-tube is fitted at the top with an overflow cup and the tube is surrounded by a bath. At the bottom of the standard oil-tube is a small outlet tube through which the oil to be tested flows into a receiving flask, whose capacity to a mark on its neck is 60 (+ 0.15) c.c. The lower end of the outlet tube is enclosed by a larger tube, which, when stoppered by a cork, acts as a closed air chamber and prevents the flow of oil through the outlet tube until the cork is removed and the test started. A looped string is attached to the lower end of the cork as an aid to its rapid removal. The bath is provided with two stirring paddles and is operated by two turn-table handles. The temperatures in the standard oil-tube and in the bath are shown by thermometers. The bath may be heated by a glass ring burner, steam U-tube, or electric heater. The standard oil-tube is cleaned by means of a tube-cleaning plunger, and all oil entering the standard oil-tube shall be strained through a 30-mesh brass wire strainer. A stop watch is used for taking the time of the flow of oil and a pipette, fitted with a rubber suction bulb, is used for draining the overflow cup of the standard oil-tube.

To make the test, heat the oil to the necessary temperature and clean out the standard oil-tube with the plunger, using some of the oil to be tested. Place the cork stopper into the lower end of the air chamber at the bottom of the standard oil-tube. The stopper should be sufficiently inserted to prevent the escape of air, but should not touch the small outlet tube of the standard oil-tube. Heat the oil to be tested, outside the viscosimeter, to slightly below the temperature at which the viscosity is to be determined and pour it into the standard oil-tube until it ceases to overflow into the overflow cup.

By means of the oil-tube thermometer, keep the oil in the standard oil-tube well stirred and also stir well the oil in the bath. It is extremely important that the temperature of the oil in the oil bath be maintained constant during the entire time consumed in making the test. When the temperature of the oil in the bath and in the standard oil-tube is constant and the oil in the standard oil-tube is at the desired temperature, withdraw the oil tube thermometer; quickly remove the surplus oil from the overflow cup by means of a pipette so that the level of the oil in the overflow cup is below the level of the oil in the tube proper; place the 60-c.c. flask in position so that the oil from the outlet tube will flow into the flask without making bubbles; snap the cork from its position, and at the same instant start the stop watch. Stir the liquid in the bath during the run and carefully maintain it at the previously determined proper temperature. Stop the watch when the bottom of the meniscus of the oil reaches the mark on the neck of the receiving flask.

The time in seconds for the delivery of the 60-c.c. of oil is the Saybolt viscosity of the oil at the temperature at which the test was made. For complete accuracy it is recommended that each viscosimeter be standardised frequently by the U. S. Bureau of Standards to avoid possible deviations in the size of exit tubes.

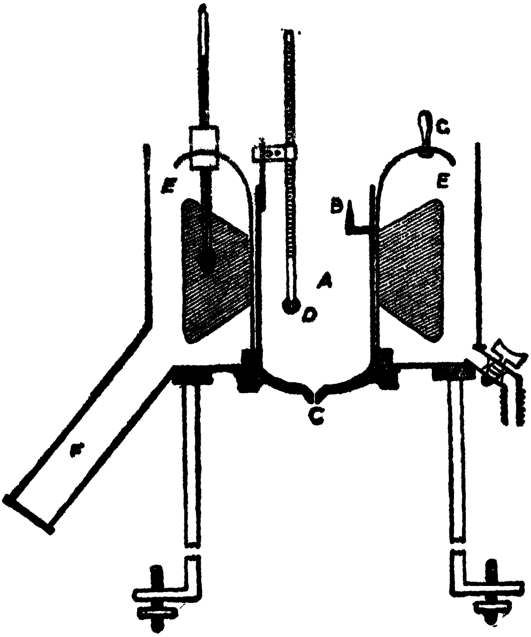

FIG. 13.—Redwood viscosimeter.

Redwood's Viscosimeter.—Boverton Redwood devised an instrument (Fig. 13) which is capable of being standardised, and has been much used. The viscosity tube (A) is made of copper thickly electroplated, and is 3½ in. high by 1⅞ in. internal diameter. In practice it is filled until the surface of the liquid just touches the point of a bent wire soldered to the side of the tube. The orifice is a hole of a definite size drilled in agate (C), but glass might doubtless be substituted without affecting the accuracy of the indications. The friction of the flowing oil against the sides of a long tubular orifice notably affects the indications of the instrument, and hence the tubular portion of the orifice is made as short as practicable. The upper surface of the agate is cup-shaped, so as to fit the bulb of the thermometer (D), which may be used as a plug, but the instrument is also supplied with a spherical plug of electroplated copper attached to a wire. The viscosity tube is surrounded by a cylindrical reservoir of copper (E), which can be filled with water or other fluid and readily brought to and maintained at any desired temperature. For temperatures below 100°, water is most convenient; above that temperature, paraffin or mineral lubricating oil of high b. p. may be used. The fluid in the reservoir may be heated by a gas-flame placed under the projecting portion (F), and can be agitated by gently moving the inclined paddles by means of the handle (H). When the temperature employed is considerably above that of the laboratory, the agitator should be kept in gentle motion throughout the experiment. Care must also be taken that the temperature of the oil in the inner cylinder is maintained constant, as a difference of 1° or less will make an appreciable difference in the rate of flow of some oils.

In using Redwood's viscosimeter, the liquid in the reservoir should first be brought to the required temperature, and the oil to be tested, previously brought to the same temperature, should then be poured into the inner cylinder until the level of the liquid just reaches the point of the gauge (B). A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball-valve is raised, and the number of seconds required for 50 c.c. of the oil to flow out is noted in the usual way. At least two experiments should be made, and the results should agree closely.

Samples should be filtered if not quite clear, as suspended matter or globules of water may obstruct the orifice. Soft paper should be used for wiping out the oil-cylinder. In employing this or similar forms of viscosimeters, it is essential that the oil should be at the same height in each experiment, and that the same measure should flow out, otherwise discordant results will be obtained. Allen made an addition to the Redwood's viscosimeter by which a constant head of oil is maintained. The oil-cylinder is provided with an air-tight cover. The cover is perforated by 2 holes fitted with short tubes, one of which is furnished with a tap, while the other has another tube screwing air-tight into it. This tube (C) is prolonged on 2 sides in contact with the agate orifice, while the angles of the inverted V-shaped slits cut on each side terminate exactly 1½ in. higher. The cylinder is filled with oil before commencing an experiment, the tap closed, and the orifice opened till the oil sinks to a certain level in the inner tube. Air then bubbles in regularly, and when this is noted, the oil is collected in a graduated cylinder. Any volume from 10 to 50 c.c. may be allowed to run out, as the oil gradually falls in the upper part of the cylinder, but is maintained constantly at the level D. Experiments made in Allen's laboratory proved the flow to be extremely regular; and the modification has the additional advantage of allowing the viscosity to be determined from the flow of a very moderate measure of oil, whereas if 50 c.c. be the volume collected, the observation sometimes becomes tedious. The results obtained by comparative testing by the closed and open apparatus agree.

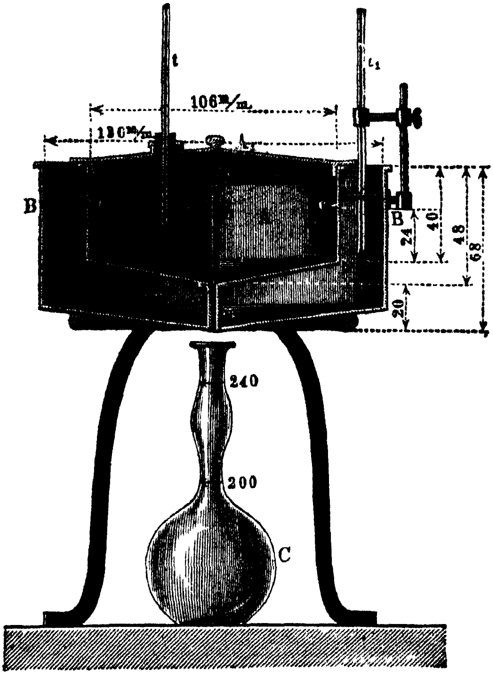

FIG. 14.—Engler viscosimeter.

Engler's viscosimeter (see Fig. No. 14) consists of an accurately made brass oil-vessel 106 mm. internal diameter. 40

mm. deep at the side, and 48 mm. at the centre, the bottom being a flat cone. A slightly conical lid, fitting snugly like a saucepan-lid, closes the vessel. The inner surface of the oil-vessel is gilded. In the centre of the bottom is a platinum outflow tube 20 mm. long, with a slightly conical calibre 2.9 mm. at the top, 2.8 mm. at the lower end. This tube can be closed by a pointed rod of hard wood. The level to which to fill the oil (240 c.c. are used) is indicated by three small pointed projections on the side of the oil vessel. A thermometer passing through a hole in the lid dips into the oil. The oil vessel is surrounded by an oil-bath 130 mm. in diameter, 58 mm. high at the sides, and 68 mm. at the centre, at which point the lower end of the outflow pipe passes through by a tight joint. The top of this bath is on a level with the top of the oil-vessel. The bath is not covered; a thermometer dips into the oil. The whole apparatus is securely supported and heated by a ring burner. A flask, marked at 200 c.c. and 240 c.c., is placed precisely below the outflow tube. To secure uniformity and obtain comparable data, standardised instruments must be employed, for the construction of which Engler has arranged with Desaga, of Heidelberg. Full directions for use are furnished with each apparatus. This viscosimeter is much used in Germany, especially in the railway service.

The quotient of the time of outflow of 200 c.c. of oil, divided by the time of outflow of 200 c.c. of water, is taken as a measure of the viscosity, or as the so-called "Engler Number."

Conversion Tables.—The Tables Nos. 6A, 6B, and 6C have been compiled by the U. S. Bureau of Standards (Technologic Paper No. 112).

TABLE 6A.—MULTIPLYING FACTORS TO CONVERT ENGLER NUMBERS TO SAYBOLT OR TO REDWOOD TIMES

Engler number	Factor to convert Engler number to Saybolt time	Factor to convert Engler number to Redwood time
1.15	29.9	26.5
1.20	30.1	26.7
1.25	30.3	26.8
1.30	30.5	26.9
1.35	30.7	27.0
1.40	30.9	27.1
1.45	31.1	27.2
1.50	31.3	27.3
1.60	31.5	27.4
1.70	31.[illegible]	27.5
1.80	31.9	27.6
1.90	32.1	27.7
2.00	32.3	27.9
2.10	32.5	28.0
2.20	32.6	28.1
2.30	32.8	28.2
2.40	32.9	28.2
2.50	33.0	28.3
2.60	33.1	28.3
2.70	33.2	28.4
2.80	33.3	28.4
2.90	33.4	28.5
3.00	33.5	28.5
3.50	33.6	28.6
4.00	33.7	28.7
4.50	33.9	28.8
5.00	33.9	28.8
6.00	34.0	28.9
7.00	34.1	28.9
8.00	34.1	28.9
9.00	34.2[1]	29.0[1]

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[1] This value holds good for all higher viscositie

TABLE 6B.—MULTIPLYING FACTORS TO CONVERT SAYBOLT TIMES TO ENGLER NUMBERS OR TO REDWOOD TIMES

Saybolt time	Factor to convert Saybolt time to Engler number	Factor to convert Saybolt time to Redwood time
34	0.0334	0.890
36	0.0332	0.886
38	0.0330	0.884
40	0.0328	0.882
42	0.0326	0.879
44	0.0324	0.877
46	0.0322	0.875
48	0.0319	0.873
50	0.0317	0.871
55	0.0315	0.869
60	0.0313	0.866
65	0.0312	0.864
70	0.0309	0.861
75	0.0308	0.859
80	0.0307	0.858
85	0.0305	0.857
90	0.0304	0.856
95	0.0303	0.855
100	0.0302	0.854
110	0.0301	0.853
120	0.0300	0.852
130	0.0299	0.851
140	0.0299	0.850
160	0.0298	0.849
180	0.0297	0.848
200	0.0296	0.848
225	0.0295	0.848
250	0.0294	0.847
300	0.0293	0.847
350	0.0293	0.847
400	0.0292[1]	0.846[1]

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[1] This value holds good for all higher viscosities.

TABLE 6C.—MULTIPLYING FACTORS TO CONVERT REDWOOD TIMES TO SAYBOLT TIMES OR TO ENGLER NUMBERS

Redwood time	Factor to convert Redwood time to Saybolt time	Factor to convert Redwood time to Engler number
30	1.12	0.0377
32	1.13	0.0375
34	1.13	0.0372
36	1.14	0.0370
38	1.14	0.0369
40	1.14	0.0368
42	1.15	0.0366
44	1.15	0.0365
46	1.15	0.0363
48	1.15	0.0362
50	1.16	0.0361
55	1.16	0.0359
60	1.16	0.0357
65	1.16	0.0355
70	1.17	0.0354
75	1.17	0.0353
80	1.17	0.0352
85	1.17	0.0351
90	1.17	0.0350
95	1.17	0.0350
100	1.17	0.0350
110	1.18	0.0349
120	1.18	0.0348
130	1.18	0.0347
140	1.18	0.0347
150	1.18	0.0347
160	1.18	0.0347
180	1.18	0.0347
200	1.18	0.0347
225	1.18	0.0346
250	1.18[1]	0.0345[1]

[1] This value holds good for all higher viscosities.

A viscosity chart, in which the equivalence of the Saybolt, Redwood and Engler readings, is shown graphically, and the relation of these readings to absolute viscosity results, has been published by H. G. Nevitt in *Chem., Met. Eng.*, 1920, **12**, 1181.

Cold Test.—Under this head the American Society for Testing Materials includes *cloud* and *pour* tests made under carefully prescribed conditions. The cloud test indicates the point at which paraffin wax or other solid substances crystallise out or separate from solution in the oil. The pour test, on the other hand, indicates the temperature at which a sample of oil in a cylindrical glass jar of specified diameter and length will just flow under specified conditions. The same glass jar and quantity of oil are used in either case. In both cases, the jar containing the oil is placed in a close-fitting metal jacket, provided at the bottom with a disc of felt or cork ¼ in. thick and then placed in the freezing mixture. A thermometer is inserted in the jar and held in position in the jar by a cork centrally bored.

In carrying out the cloud test, at every drop of 2° F. in the temperature, when near the expected cloud test, remove the jar from the jacket and inspect, being careful not to disturb the oil by moving the thermometer or otherwise. When the lower half of the sample becomes opaque through chilling, read the thermometer. This reading is taken as the cloud test. In making the pour test, place the jar containing the oil in a close-fitting metal jacket as before described. At each drop in temperature of 5° F. remove the bottle from the jacket and tilt it until the oil begins to flow. The bottle is tilted just sufficiently but no more, in no case beyond the horizontal. When the oil has become solid around the thermometer and will not flow, the previous 5° point shall be taken as the pour test.

Flash and Fire Test.—This, in the case of lubricating oils, may be determined by either the open cup method or a closed cup of the Pensky-Martin type. The open cup generally in use is the Cleveland instrument. This consists of a brass cup holding 100 c.c., supported in an outer vessel with an air space between. The thermometer is suspended freely in the oil under test, so that the bulb is covered. The cup is filled to ¼ in. from the top, and the oil is heated at the rate of 10° F. per minute. As the flash-point is approached, the test flame (5 mm. in length) is moved slowly back and forth so that the top of the flame comes within 2–3 mm. from the surface of the liquid without, however, touching it or the sides of the container. This is repeated every 2° F. rise in temperature until the vapours flash.

The Pensky-Martin closed cup tester is described in "Methods for Testing Petroleum Products," Technical Paper 298, of the U. S. Bureau of Mines, 1922, and is the form adopted by the American Society for Testing Materials.

In carrying out the test, the cup is filled with the oil to be tested up to the level indicated by the filling mark. The lid is placed on the cup and the latter set in the stove. Care must be taken to have the locating devices properly engaged. The thermometer is inserted. If it is known that the oil will flash above 220° F., the high temperature thermometer may be selected; otherwise it is preferable to start with the low temperature thermometer and change in case a temperature of 220° to 230° F. is reached.

The test flame is lighted and adjusted so that it is 5/32 in. (3.97 mm.) in diameter. Heat is supplied at such a rate that the temperature read on the thermometer increases not less than 9 nor more than 11° F. per minute. The stirrer is turned at a rate of from 1 to 2 revolutions per second. Application of the test flame is made at each temperature reading which is a multiple of 2° F. up to 220° F. For the temperature range above 220° F., application shall be made at each temperature reading which is a multiple of 5° F. Application of the test flame is made by operating the device controlling the shutter and test flame burner so that the flame is lowered in one-half second and quickly raised to its high position. Stirring is discontinued during the application of the test flame. The flash-point is taken as the temperature read on the thermometer at the time of the flame application that causes a distinct flash in the interior of the cup. The barometric pressure is recorded, but no correction need be made except in case of dispute, when the flash-point figures may be corrected as follows: for each inch (25 mm.) below 29.92 in. (760 mm.) barometric reading add 1.6° F. to the flash-point. For each inch (25 mm.) above 29.92 in. (760 mm.) barometric reading subtract 1.6° F., from the flash-point.

Free Acids.—Sulphuric acid not removed during refining, free fatty acids present in the fatty oils used in compounding, rosin oils, or oxidation products may be the cause of acidity in lubricating oils. First class lubricants should be free from not only the petroleum acids and sulphuric acid, but also sulphonates. The acidity is expressed in the number of milligrams of potassium hydroxide necessary to neutralise 1 grm. of the oil. The method of the American Society for Testing Materials is to titrate the oil mixed with pure neutralised ethyl alcohol with aqueous N/10 potassium hydroxide, with phenolphthalein as indicator.

Fatty (Saponifiable) Oil.—The method of the American Society for Testing Materials is as follows: solutions required—approximately N/2 alcoholic potassium hydroxide, purified benzene, standard solution of N/2 hydrochochloric acid, phenolphthalein indicator and neutral gasoline. Weigh 10 grm. of oil into a 350 c.c. Erlenmeyer flask. Add from a pipette 50 c.c. of the alcoholic potassium hydroxide solution, followed by 25 c.c. of the purified benzene (C_6H_6). Connect with return condenser. Boil on steam bath or electric hot plate for 90 minutes, shaking occasionally. Remove and add 25 c.c. of neutral gasoline and titrate with the N/2 hydrochloric acid solution, after adding 2 or 3 drops of the phenolphthalein indicator solution, until the pink colour is destroyed. The absence of the pink colour may be determined after the titration has begun by allowing the solution to rest approximately a minute and noting the colour of the lower zone. Run two blanks with the same mixture of alcoholic potassium hydroxide solution and purified benzene. From the difference between the number of c.c. of N/2 hydrochloric acid for the blanks and for the determination, the percentage of fatty oil may be calculated as follows:

$$\frac{\text{No. of c.c. N/2 acid used} \times 0.02805 \times 100}{0.195 \times \text{weight of oil taken}}$$

A qualitative test for the presence of a fatty oil may be made as follows: heat a small quantity of the oil in a test-tube with metallic sodium or solid potassium hydroxide. If a fatty oil is present, in the former case the oil will gelatinise, whilst in the latter instance a froth will be produced on the oil in addition to gelatinisation.

Emulsification Tests.—For many uses a non-emulsifiable oil is essential. An oil which will emulsify with water contains some substance which acts as the emulsifying agent. Examples of emulsifiers are salts of organic acids, such as the calcium and magnesium salts of the fatty acids, sulphonates and the salts of naphthenic acids.

The resistance of an oil to emulsification is known as the *demulsibility.* The U. S. Bureau of Mines method (*Technical Paper* 298 *Bureau of Mines*, p. 43) is as follows: the apparatus required is a 100 c.c. graduated cylinder standing immersed in an oil or water bath and a paddle consisting of a copper plate attached to a vertical stem which can be revolved at a speed of 1500 r.p.m.

Place 27 c.c. of the oil to be tested and 53 c.c. of distilled water in the cylinder and heat the cylinder by means of the bath to 130° F. (or other chosen temperature), stir by rotating the paddle for 5 minutes at a speed of 1500 r.p.m., stop the paddle, withdraw from the cylinder and wipe clean, returning to the cylinder as much of the emulsion as possible. Keeping the temperature of the cylinder constant, take readings every minute of the position of the line of demarcation between the topmost layer of oil and the adjoining emsulsion. Take the first reading 1 minute after stopping the paddle. With oils which act normally, the rate of settling out of the oil increases up to a maximum value in cubic centimeters per hour and then decreases. The maximum figure is taken as the "demulsibility" and recorded as the result of this test. Each rate of settling is the average rate calculated from the time of stopping the paddle to the time of reading as shown in the following condensed table.

METHOD OF COMPUTING RATE OF SETTLING

Time	Time since stopping paddle, minutes	Reading at interface, between oil and emulsion	Oil settled out, cubic centimeters	Rate of settling per hour, cubic centimeters
9.50	0	80	0	0
9.55	5	77	3	36
10.02	12	67	13	65
10.05	15	63	17	68
10.10	20	61	19	57

In this case the demulsibility figure of the test would be 68. A somewhat similar method for determining demulsibility has been proposed by Conradson in which steam is blown into a mixture of oil and water placed in a cylinder and the degree of after separation measured (*Hamor and Padgett, Examination of Petroleum*, 109).

Carbon Residue Test.—The method of Conradson, very largely in use, is as follows: a porcelain crucible, wide form, glazed throughout and of 25 to 26 c.c. capacity is placed in a Skidmon iron crucible of 45 c.c. capacity, provided with cover, without delivery tubes and with one opening closed. This in turn is placed in a wrought iron crucible also with cover, on the bottom of which a layer of sand is placed. 10 grm. of the oil to be tested are weighed in the porcelain crucible, which is placed in the Skidmon crucible, and this latter placed centrally in the larger iron crucible. The outer crucible being supported on a pipe stem covered triangle, heat is applied from a Bunsen burner so that the flame surrounds the large crucible. When vapours from the oil come off and ignite over the crucible, the flame is to be controlled so that the vapours burn at a uniform rate. When the vapour ceases to come off, the heat is to be increased as at the start and kept so for 5 minutes, making the lower part of the large crucible red hot, after which the apparatus is to be allowed to cool. The porcelain crucible is then removed, cooled in a descicator and weighed. This process has been adopted by the American Society for Testing Materials.

Precipitation Number.—The American Society for Testing Materials precipitation number is the number of cubic centimeters of precipitate formed when 10 c.c. of lubricating oil are mixed with 90 c.c. of petroleum naphtha of definite quality and centrifuged under definite prescribed conditions. The method is commonly used for steam cylinder stocks and black oils and may be used for other lubricating oils. (For details see *Technical Paper* 298 *of the Bureau of Mines*, p. 40.)

Mineral matters can be detected in the residue left on igniting the oil. *Free alkali* can be estimated by titrating the oil in presence of alcohol with standard acid and phenolphthalein, and that existing as *soap* by using methyl-orange as an indicator. *Aluminium palmitate* and *oleate* are now added to mineral oils to increase viscosity. A mixture of mineral oil with about 10% of aluminium soap is sold largely under the misleading name "gelatin."

For the detection of these Schweitzer and Lungwitz (*J. Soc. Chem. Ind.*, 1894, **13**, 1178) have devised the following test: about 0.5 c.c. of the sample is dissolved in 5 c.c. of petroleum spirit (boiling below 75°) anhydrous ether or absolute alcohol, and mixed with 1 c.c. of a saturated solution of metaphosphoric acid in absolute alcohol or anhydrous ether. In the presence of potassium, sodium, magnesium, or aluminium a precipitate is formed. The reaction depends on the fact that, while metaphosphoric acid is soluble in absolute alcohol or ether, most of its salts are insoluble. The reagent may be prepared by shaking the powdered metaphosphoric acid with absolute alcohol, allowing the mixture to stand until clear, and pouring off the solution. It must be kept tightly stoppered.

Calcium oleate is not infrequently added to, or formed in, mineral lubricating oils. (See Lubricating Greases.)

Rosin oil is detected in mineral oils by a method of Allen, which consists in dissolving a few drops of the oil in question in 1 c.c. of carbon disulphide solution of stannic bromide containing an excess of bromine.

According to Redwood, Finkener recommends the use of a mixture of 1 volume of chloroform and 10 volumes of alcohol of 0.818 sp. gr. for separating rosin oil from mineral oils. 10 volumes of this mixture (at 23°) will dissolve 1 volume of rosin oil from admixture with mineral oils without taking up any appreciable quantity of mineral oil.

A method for the quantitative estimation of rosin oil in mineral oils, given by P. C. McIlhiney (*J. Amer. Chem. Soc.*, 1894, **16**, 385–8), is based on the principle that the action of nitric acid on rosin oil converts it into a brittle red resin and does not act on petroleum hydrocarbons. This resin is not dissolved by petroleum spirit, which removes petroleum products. The details of the method are as follows:

50 c.c. of nitric acid (sp. gr. 1.2) is brought to boiling in a flask of 700 c.c. capacity. The flame is then removed and about 5 grm. of oil (noting exact weight) is then dropped in. The flask is heated for 15 or 20 minutes on the water-bath and then 400 c.c. of water added. When cold the contents of the flask are treated with petroleum spirit which dissolves all mineral oils and leaves the altered rosin oil. The difference in weight between the mineral oil recovered and the oil taken, gives the amount of rosin oil in the sample.

The **fluorescence** or "bloom" of mineral lubricating oil may sometimes be destroyed by exposure to light, but more rapidly and certainly by subjecting it to a process of limited oxidation by treatment with nitric acid. Turmeric, α-nitronaphthalene, and picric acid also obscure the fluorescence. Dinitrotoluene is much used in the proportion of 4 pounds to the ton of oil. There are, however, varieties of commercial mineral lubricating oils wholly non-fluorescent, and in which the property cannot be developed by any known treatment.

Deblooming Agents.—As a general preliminary test, Holde (*J. Soc. Chem. Ind.*, 1894, **13**, 906) advises the following: the clear oil is boiled for from 1 to 2 minutes in a test-tube with about 3 c.c. of concentrated alcoholic solution of potassium hydroxide. Oils containing nitro-compounds become blood-red or violet-red, and on warming the upper part of the tube where there are adhering drops of the alkaline solution, just above the main bulk of the liquid, these drops become at once reddish-violet. Holde has never observed the latter reaction with any oils not containing nitro-derivatives, but some fatty oils will produce, on long heating, a yellowish-red or blood-red in the body of the liquid, although the usual colour is a merely brownish.

For the detection of α-nitronaphthalene, used as a deblooming agent, N. Leonard (*Chem. News*, 1893, **68**, 297), has devised the following method, depending upon the production of α-aminonaphthalene, which has a characteristic disgusting odour, similar to that of a decayed tooth.

A small quantity of the oil is gently warmed with zinc dust and dilute hydrochloric acid, and the mixture shaken from time to time. If α-nitronaphthalene be present, the odour of the amino-derivative will be noted. When the reduction is complete, the acid water is withdrawn by a separatory funnel. A portion of this liquid, neutralised by ammonium hydroxide, will give, with ferric chloride, a blue precipitate, becoming purple. The remainder of the solution may be rendered alkaline with sodium hydroxide and extracted with ether, the ether evaporated, the residue dissolved in a little alcohol, and to this solution a drop of a solution of sodium nitrite, acidified with acetic acid, is added. A yellow coloration is produced, which is changed to crimson by hydrochloric acid.

Mineral oils are sometimes compounded with caoutchouc. For the detection of this, Holde (*J. Soc. Chem. Ind.*, 1891, **10**, 390) advises the following: ascertain the solubility by shaking 1 volume of the oil with 2 volumes of alcohol, benzene, or ether; precipitate the caoutchouc by treating the oil with a mixture of 3 parts ether and 4 parts alcohol. The precipitate is filtered out, washed, dried, and weighed.

The following classification of mineral lubricating oils (Thomsen, Practice of Lubrication, p. 11) will be found convenient.

Dark Cylinder Oils.—Dark cylinder oils are the undistilled dark residues left in the stills (by steam distillation, chiefly of non-asphaltic crude), freed from solid impurities, but not filtered. They are chiefly used for lubrication of steam engine cylinders and valves, either alone or mixed with from 3 to 10% of acidless tallow oil.

Filtered Cylinder Oils.—Filtered cylinder oils are made from dark cylinder oils by filtration. They represent the highest quality oils used for internal lubrication of steam engines; they are used either alone or mixed with from 3 to 12% of acidless tallow oil. They are also largely used for mixing with lower viscosity oils to produce heavy viscosity oils for internal combustion engines, or *heavy* *viscosity* engine and machinery oils, air compressor oils, circulation oils, etc.

Red Oils.—Red oils are fire-distilled (with or without steam), acid-treated oils. They represent a large portion of the medium and heavy viscosity oils used for general lubrication of engines, shafting and machinery of all kinds. Mixed with filtered cylinder oil, red oils produce very heavy viscosity engine and machinery oils.

Red oils, made from paraffin base crude, are not very satisfactory for making oils for internal combustion engines, as they produce a great deal of hard and brittle carbon. When made from asphaltic base crudes, they produce less carbon deposit and it is of a soft crumbly nature.

The heavy red oils, when mixed with from 5 to 20% of fixed oil (blown or unblown), produce some of the lighter viscosity marine and railway engine oils.

Pale Oils.—Pale oils are fire-distilled (with or without steam), heavily acid-treated or heavily filtered oils. They are of light to medium viscosity, and are used for lubricating quick-running machinery, such as high speed shafting, electric motors, textile machinery, also for manufacturing yellow lubricating greases. Further, they are used largely for lubricating small and medium sized internal combustion engines of all kinds, either alone or mixed with from 3 to 10% of fixed oil, or filtered cylinder oil (when a heavy viscosity oil is required).

Pale oils produce less carbon deposit than red oils when used for lubricating internal combustion engines.

Neutral Oils.—Neutral oils are steam or fire distilled oils (freed from paraffin wax, if wax is present), sun-bleached and filtered through fuller's earth and when not acid-treated are called filtered neutral oils. Most neutral oils are filtered rather than acid-treated.

Neutral oils are of light or medium viscosity and used for similar purposes as pale oils; neutral filtered oils are more suitable than pale oils for self-oiling bearings, where the oil is used over and over again. Neutral filtered oils are largely used as circulation oils (for enclosed type steam engines and steam turbines) either alone or mixed with filtered cylinder oil, as they separate well from water.

Bloomless Oils.—Bloomless oils are neutral oils which have been highly filtered and may also have been sun-bleached; they are very light in colour and of light viscosity.

To remove the bloom entirely they must be treated with nitronaphthalene or other chemicals.

Bloomless oils are used for adulterating edible oils; also in the manufacture of stainless loom and spindle oils.

White Oils.—White oils are pale spindle oils which have been treated with fuming sulphuric acid or liquid sulphur dioxide, fuller's earth filtration, etc.; in order to remove the colour completely. They are easily made from Russian crudes and are largely used as non-sludging transformer oils. It is very difficult to remove colour entirely from oils produced from paraffin base crudes.

Medicinal White Oils.—Medicinal white oils are white oils which have been so treated as to remove not only colour but also all taste and odour.

LUBRICATING GREASES

Greases or "consistent lubricants" are generally colloidal solutions of soaps in lubricating oils, along with a small quantity of water dispersed through the mass. The water, which is in a state of emulsification in the oil, makes possible the peculiar consistency of the product as well as prevents separation of the colloidal soap. Some greases however do not contain water. Straight soda greases, for example, are oils thickened by the addition of soda soaps to the extent oftimes of 50%, but no water.

The tests under this heading are according to Gillette (*J. Ind. and Eng. Chem.*, 1909, 1, 351).

In the analysis of a grease, the following points may be covered:

Consistence.

M. p.

Flash point.

Content of free acid.

Amount and nature of soap.

Ash, not alkali, from soap, nature and amount.

Mineral filler, as graphite, talc, etc., nature and amount.

Content of unsaponified, but saponifiable animal or vegetable fats or oils, nature and amount.

Content of unsaponifiable mineral or hydrocarbon oil, nature and amount.

Content of water.

The methods used in the analysis of the grease are as follows:

Note first the odour and colour. These may give clues of the probable composition, and will show if the grease is perfumed with nitrobenzene or any other similar substance. Note the behaviour on melting. The grease should melt to a clear homogeneous fluid. The oil should not melt away from the soap, since in such a case, after being in the feed cup some time, the grease may change in composition, the oil running off the bearing and the soap staying behind.

The consistence at 20° was determined by a Legler consistometer which consists of a pointed glass rod, bearing a pan for weights, and supported by a spiral spring (*Chem. Ztg.*, 1884, **8**, 1657; *Chem. Ctrbl.*, 1884, **15**, 734. Benedict and Lewkowitsch "Oils, Fats and Waxes," 1921, Ed., p. 369).

The grease was maintained at 20° for about an hour, and the total weight determined which was required to sink the rod into the grease exactly 1 cm. The spring was of such strength that it took 20 grm. to depress the rod 1 cm. in air, and this 20 grm. was subtracted from the total weight required, to give the consistency number. This varied in different commercial greases from 200 grm. to 4 grm. Readings could be checked to within 5% of their value. The instrument gave a consistency number for the pasty mass consisting of 50% stearic and 50% oleic acids, of 75–80 grm. All the weights must be on the pan before it is released, as the penetration is less if the weights are added while the rod is falling. The measurement of the consistence is a well-recognised part of the examination of a lubricating grease (Benedict and Lewkowitsch, *Loc. cit*, Archbutt and Deeley, "Lubrication and Lubricants," 2d Ed., p. 170) yet it has no direct bearing on the lubricating power. Its value lies chiefly in showing what sort of grease cup should be used for that particular grease, whether gravity, compression, etc.

The m. p. is the most important single determination, as will be seen in the discussion of the friction tests.

Ubbelohde[1] gives a method for greases melting below 100°. Gillette found the most satisfactory method to be the use of an open tube of 0.4 cm. internal diameter, and about 8 cm. long. This is stuck into the grease so that a plug of grease 1 cm. long is left in the glass tube. The tube is then attached by a rubber band to a thermometer so that the plug is beside the bulb. The thermometer, with the tube attached, is then immersed into a beaker of water so that the bottom of the plug is 5 cm. below the surface. The water is then heated at the rate of 3 to 4° per minute. When the m. p. is reached, the plug, which is under a pressure of 5 cm. of water, slides upward in the tube. Checks can be obtained to 0.5°.

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[1] Holde, "Untersuchung der Mineralöle und Fette," Berlin, 1905, p. 209.

The effects of varying the different conditions of this test have been investigated by Gillette.

The flash-point is taken in a 50 c.c. porcelain crucible filled with the grease, into which is stuck the bulb of a thermometer. The crucible is heated at 5° per minute on a sand-bath, and the flash determined by noting the temperature at which a 3 mm. gas flame passed over the crucible at 2° intervals causes a flash to pass over the surface. The chief value of this determination is to give some idea of the grade of mineral oil used in compounding the grease.

Free Acid in Lubricating Greases (*Holde-Muller*, 4th Ed., p 192).—Due to the presence of metallic soaps in lubricating greases and their tendency to dissociate in the presence of water, and particularly solutions of alkali hydroxides, the ordinary methods of estimating free acids do not apply. Holde has worked out the following method: 10 grm. of the grease are boiled under reflux with a mixture of 90 volumes of 88° gasoline and 10 volumes of absolute alcohol until dissolved. The solution is filtered off from the insoluble soaps and the latter is washed with the same solvent mixture. Add 20 c.c. of 50% alcohol (neutralized to phenolphthalein) and titrate with N/10 KOH in the presence of phenolphthalein. Most commercial greases run almost neutral, 0.5% being high, though as high as 6% has been found. Greases that contain unsaponified palm oil are especially likely to show free acid. The importance of neutrality is very great, because of the corrosion of the bearings by free acid.

Soap.—The estimation of the soap content may be made in several ways. The bases may be thrown as oxalates from a turpentine-benzene-alcohol solution by oxalic acid, after the method of Conradson (*J. Amer. Chem. Soc.*, **26**, 6, 705), and the soap content calculated from the amount of base found. The soaps may be determined by Holde's method of decomposing the soaps by mineral acid, washing out the mineral acid, and titrating the fatty acids thus freed, and from the titration figuring the amount of soap.

The simplest and shortest method, however, in practically every case, is to ash the grease, titrate the Na_2CO_3, K_2CO_3, or CaO in the ash with acid, and calculate the soap content from the titration, 1 c.c. of N/2 acid being equivalent to

0.1612 grm. potassium stearate.
0.1535 grm. sodium stearate.
0.1520 grm. calcium stearate.

If the Liebermann-Storch rosin test shows the soap to be partly rosin soap and rosin oil is absent, this will give low figures, owing to the higher combining weight of abietic than that of stearic or oleic acids. In such a case, if extreme accuracy is required, the fatty acids of the soaps may be freed, and rosin estimated by Twitchell's method. Ordinarily this would not be required.

In the case of greases made with sodium or potassium soaps, the soap may be directly estimated, after extraction in a Soxhlet of the unsaponified and unsaponifiable fats with ether, by extraction of the residue from the ether extraction, with alcohol. With lime soaps this fails, owing to the large solubility of calcium soap in all solvents for fats, as well as its insolubility in alcohol. It would greatly simplify the analysis of greases containing calcium soap if some solvent could be found that would extract fats and oils without extracting any of the lime soap, in the same way that ether may be used to separate the fats and oil from the soap in a soda soap grease. In attempting to make an ether extract of a lime soap grease, the author has repeatedly found from ¼ to ⅓ the total lime in the ether extract, owing to the solubility of calcium soap. Gasoline extracts nearly as much. Numerous experiments have been made with other solvents and mixtures of solvents, but no satisfactory one has been found. Ethyl acetate at room temperature dissolves but little of the calcium soap, and the extract will give a fair qualitative idea of the nature of the oil used in compounding the grease.

If the grease is made up with a lead soap, the lead may be determined by decomposing the grease by boiling with a mixture of sulphuric and nitric acids, after the Neumann acid ashing method, and weighing the lead sulphate.

The nature of the base used in the soap may be determined by the usual methods, or more quickly and delicately by microchemical methods. A small amount is ignited on a porcelain crucible cover, the ash dissolved in dilute HCl and 3 drops of the solution put on a microscope slide. To the first drop is added a small drop of dilute H_2SO_4, and to the second a small drop of H_2PtCl_6. The third is evaporated to dryness over a micro-burner, and a drop of concentrated solution of uranium acetate, slightly acidified with acetic acid, is added. The 3 drops are then examined under the microscope. The first will show the characteristic sheaf-like groups of gypsum crystals if lime is present, or the fine white granular plates and rhombs of $PbSO_4$ if lead is the base used. The second will show the yellow octahedra of K_2PtCl_6 if potassium is present, while the third drop will show the tetrahedra of the double acetate of uranium and sodium, if a soda soap.[1]

Ash.—The amount of ash other than alkalies from the soap maybe determined by the difference between the total ash and the alkali found by titration. Greases contain from zero to sometimes 1% of adventitious dirt, iron and aluminium oxides, silica, etc.

In the case of a grease containing graphite, talc, etc., the mineral filler may be estimated directly after extraction with ether and then with alcohol, if an alkali soap, or in any case, by weighing the ash insoluble in acid. In the case of graphite, care should be taken to ash at a low temperature to minimise the oxidation of the graphite.

The unsaponified saponifiable matter, in the case of a grease made with an alkali soap, is best determined by saponification of the ether extract with alcoholic potash. The nature of the saponifiable may be found by evaporating off the alcohol after saponification, extraction of the unsaponifiable with ether, freeing the fatty acids from the soap left behind, and taking the m. p., iodine value, and refractive index of the fatty acids, and thus identifying the fat from which the acids come. This is simple if only a single fat was used, but less so in a mixture. In most cases where a grease contains unsaponified saponifiable matter, it has been made by a partial saponification of the fat in question, and so the original grease may be saponified directly and the total fatty acids examined.

In a calcium soap grease, the soap may be decomposed by heating with a little dilute HCl, washing, saponifying the freed fatty acids with alcoholic soda, evaporating the alcohol and extracting the mixture of soda soap and unsaponifiable, which is now in the condition of a grease originally made with soda soap, with ether. This gives the unsaponifiable, and the examination of the fatty acids in the soap may be made as above. The unsaponifiable ether extract will consist of mineral or hydrocarbon oil, and the sp. gr. flash-point, and refractive index will show the nature of the mineral stock. In a rosin-oil grease the mixture of rosin oil and mineral oil may be treated by any of the usual methods for quantitative separation or estimation, none of which, however, is very satisfactory.

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[1] For a full description of these extremely delicate and rapid microchemical methods which are so valuable but so little known, see Behrens, Microchemische Analyse, or a series of articles by Chamot in *J. App. Microscopy*, Vols. 3, 4.

The estimation of water in lubricating greases is usually made either by the delightfully simple method of "determination by difference" or by drying down to constant weight. Archbutt and Deeley ("Lubrication and Lubricants," p. 306) advocate drying at 105° to 110° until frothing ceases. Wright ("Analysis of Oils and Allied Substances," p. 104) drys at 105° till the weight is approximately constant at half-hour intervals of weighing. Hurst ("Lubricating Oils, Fats and Greases," p. 281) drys at 220° F. to constant weight. Conradson (*J. Amer. Chem. Soc.*, 1904, **26**, 6, 705) takes moisture by difference, but recognised the fact that some oil is volatile at 100°. Holde ("Untersuchung der Mineralole und Fette," 2d Ed., p. 213) says: "The old method of mixing a weighed portion with alcohol, heating till no more bubbles appear, cooling and weighing, only gives useful results in the absence of light volatile oils. More general is the application of the Marcusson xylene method.[1] By this method 6 greases gave from 1 to 6.3% water, the difference between checks on the same grease being 0 to 0.2%. By other methods the water content came from 0.5 to 2.2% too high."

Attention was first drawn to this in the laboratory of the American editors by a series of greases rather high in water content which were dried in the water-oven to an apparent constancy of weight, but lacked several per cent. of adding up to 100. On investigation it was decided that the water estimation was the weak point, and determinations were made by the xylene method, when the analyses added up satisfactorily. Further work showed that though in this case the moisture estimations by drying were too low, in general drying to constant weight gives high results, as claimed by Holde.

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[1] J. Marcusson, 1904. "Bestimmung des Wasser- und Säurengehaltes von Schmierfetten." *Mitt. K. Materialsprüfungsamt*, 24, 48; "Von die Bestimmung des Wassergehaltes von Oelen, Fetten, Seifen, Harzen, u.s.w.," *Mitt. K. Mater.*, 23, 58. See also Hoffman, *Z. angew. Chem.*, 21, 2095; *Chem. Abstr.*, 3, 2, 158 (Jan. 20, 1909). See page 110 for description of method of distillation with naphtha.

To estimate the moisture in a lubricating grease, first test it with anhydrous $CuSO_2$ if the grease is sufficiently light in colour. If water is present, or in the case of a dark grease, 10 grm. are weighed out on a balanced filter-paper, the grease and paper are placed in a 300 c.c. Erlenmeyer flask and are covered with xylene. The xylol should be distilled from water and separated out from the water after clearing in a separatory funnel. The flask, connected with a dry condenser, is heated in a bath of cylinder oil, and the xylene and water slowly distilled off till the xylene comes over clear. The bulk of the water comes over with the first 10 c.c. of distillate. The distillate may be caught in a burette filled with water up to the lowest graduation, best with a few drops of xylene added to give the same meniscus as will be read, or in a receiver made like a funnel, with a graduated stem closed at the bottom, according to the method of Dean (A. L. Dean, "The Estimation of Moisture in Creosote Wood." Forest Service Circular, 134, Jan., 1906), and allowed to stand overnight, or until all milkiness had disappeared. A still better and more rapid method is to catch the distillate in centrifuge tubes, such as are used in urine analysis. The fine graduations allow of very accurate reading. Bulbs holding about 50 c.c. are blown on the tops of these tubes, and the modified tubes containing the xylene-water mixture whirled in a larger centrifuge than the one they were designed for. This obviates the necessity of waiting for the xylene to clear. A complete moisture estimation may be made in 45 minutes.

Absolute accuracy in the estimation of water in the technical examination of lubricating greases is doubtless not important, though Holde has shown (Holde, "The Physical Condition of Solid Fats, and of Solutions of Calcium Soaps in Oil." *Petroleum*, 4, (I), 14, Oct. 7, 1908) the great influence exerted by even 1% of water on the drop-point and the emulsified condition of lime-soap greases. Everyone who has driven off the water from a lime-soap grease containing a few hundredths of a per cent. of water has noticed the change from a buttery opaque mass to a gelatinous translucent one. Although not particularly important in the case of greases, the fact that the xylol method gives more accurate results than that of drying down is of importance in the analysis of other commercial products containing water.

13 commercial greases were analysed according to the methods given above, with the following results:

TABLE I

No.	Name	Flash-point °	Consistence, grm., 20°	M. p., °	% calcium soap	% other thickeners
1	Graphite	195	18	93	11	16 % graphite.
2	Summer motor	160	170	87	38	...
3	Winter motor	175	7	86	23	...
4	K 1	193	24	85	16	...
5	K 2	195	66	93	20	...
6	Auto	190	11	79	19	...
7	Tallow A[1]	210	150 (estimated)	52	...	1.4 % potash soap.
8	Table XX[1]	115	200	49	...	2.1 % potash soap. 30 % paraffin.
9	Lead rosin oil	240	7	102	...	1.75 % lead.
10	Lime rosin oil	198	31	77	...	9.9 % CaO.
11	Lime rosin oil	198	4	75	...	7.8 % CaO.
12	Soda grease	215	35	83	...	22 % sodium soap.
13	Non-fluid oil	210	27	76	9.8	12.9 % sodium soap.
14	No. 4 petrolatum	247	6	47	...	...
15	Lard oil	265	0	5	...	...

TABLE. II.—(*Continued*)

No.	Name	% H_2O	% saponifiable oil	% acids as oleic	% mineral oil
1	Graphite	Trace	17	0	56
2	Summer motor	0.05	25	Trace	36.5
3	Winter motor	0.03	37[2]	6.1	40
4	K 1	0.2	16	0	67
5	K 2	0.3	20	0.3	60
6	Auto	1.0	20	Trace	60
7	Tallow A[1]	2.5	73.5	0	22
8	Tallow XX[1]	Trace	48	0	20
9	Lead rosin	24.7	0	0	...
10	Lime rosin	Trace	0	0	...
11	Lime rosin	20.0	0	0	...
12	Soda grease	0.0	0	0	78[3]
13	Non-fluid oil	0	7	0	70.3
14	No. 4 petrolatum	0	0	0	100
15	Lard oil	0	100	..	0

[1] Scented with nitrobenzol. [2] Chiefly palm oil. [3] Oil of 24.2° Bé.

PETROLATUM (PETROLEUM JELLY—VASELINE)

Bacon and Hamor (Amer. Pet. Ind., Vol. 2, p. 632) thus describe the manufacture of this product. Vaseline-like products are now made to some extent from residues, but more largely from what are termed steam-reduced amber crudes or suitable crude oils from which the lighter fractions, including the lubricating oils, have been removed by steam distillation. The reducing is sometimes carried out under diminished pressure by what is termed the "vacuum process," when the reduced oils can be brought to 337.7° (640° F.) fire test without acquiring the slightest pyrogenous odour.

The "reduced oils" are filtered through well-dried granular animal charcoal or fuller's earth in steam-jacketed filters or in chambers kept at from 110° to 130° F., or in some cases higher. The first runnings from the filters are colourless and then pass from a light straw or amber colour to a colour which is red by transmitted light and light green by reflected light. The latter product is known as "cylinder stock" or "filtered cylinder oil" and is collected for use as a lubricating oil. The clearer portion of the filtrate may then be brought to the proper melting point, if necessary, by the addition of steamed rod wax (or amorphous paraffin obtained from oil well deposits) which dissolves perfectly in the warm liquid oil. The commercial varieties of petrolatum may be classed under two heads: (1) those which, like vaseline, are obtained as a ready formed mixture of hydrocarbons of gelatinous consistence; (2) those made by directly mixing solid paraffin of low melting point with heavy lubricating oil, such as are known in Germany as "artificial vaselines." The latter varieties are less homogeneous and are liable to deposit granules of paraffin on keeping; they are therefore not so suited for the preparation of ointments as true American Petrolatum.

In the U. S. Pharmacopœia (9th Rev.) there are three forms of petrolatum, *viz.*: **Petrolatum, Petrolatum Album,** and **Petrolatum Liquidum.** In the British Pharmacopœia there are three, as follows: **Paraffinum Liquidum, Paraffinum Molle** and **Unguentum Paraffini.** The Liquid Paraffin of the German Pharmacopœia is obtained from heavy fractions of petroleum by successive treatments with 66° Be. sulphuric acid and oleum. These destroy all unsaturated constituents and leave a mixture of saturated hydrocarbons resembling melted paraffin wax.

In 1915, when the Russian supply was cut off, the manufacture of liquid petrolatum or "white medicinal oil" was started on a large scale in the United States, and a number of products claimed to be equal to the "Russian white oil" are now being marketed, using both paraffin-base petroleum and the California crude containing naphthene.

According to Mabery (*Proc. Am. Acad.*, 1904, **40**, 361) vaseline consists of heavy oils of the series C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4} with solid paraffin hydrocarbons, the latter being in sufficient quantity to saturate the former and produce an emulsion.

The U. S. Pharmacopœia describes **Petrolatum** as follows: petrolatum is an unctuous mass varying in colour from yellowish to light amber, having not more than a slight fluorescence, even after being melted; it is transparent in thin layers; completely amorphous; free or nearly free from odour or taste.

Petrolatum is insoluble in water, almost insoluble in cold or hot alcohol, or in cold dehydrated alcohol; freely soluble in ether, chloroform, carbon disulphide, oil of turpentine, petroleum benzine, benzene, or in most fixed or volatile oils.

Sp. gr. 0.820 to 0.865 at 60°. It melts between 38° and 54°. Heat about 2 grm. of petrolatum in an open porcelain or platinum dish, over a Bunsen flame; it volatilises without emitting an acrid odour, and on incineration not more than 0.05% of ash remains.

Shake melted petrolatum with an equal volume of hot distilled water; the latter remains neutral to litmus (**acids** or **alkalies**).

Digest 10 grm. of petrolatum at 100° for half an hour with 10 grm. sodium hydroxide and 50 c.c. of distilled water; then separate the aqueous layer and supersaturate with sulphuric acid; no oily or solid substance separates (**fixed oils, fats** or **rosin**).

Petrolatum liquidum of the U. S. Pharmacopœia may vary somewhat in viscosity as well as in sp. gr., and two grades are mentioned. "Heavy liquid petrolatum has a viscosity of not less than 3.1 when determined by tests given below." "Light liquid petrolatum has a viscosity of not more than 3 when determined by the test given below and vaporises freely."

"Sp. gr. for Liquid Petrolatum 0.828 to 0.905 at 25°.

A colourless transparent oily liquid, free or nearly free from fluorescence, odourless and tasteless when cold and possessing not more than a faint petroleum odour when heated.

When cooled to 10°, liquid petrolatum does not become more than opalescent (**solid paraffins**).

Insoluble in water or alcohol; soluble in ether, chloroform, petroleum benzine, or in fixed or volatile oils. Camphor, menthol, thymol and many similar substances are dissolved by liquid petrolatum.

Boil 10 c.c. of liquid petrolatum with an equal volume of alcohol; the alcoholic liquid is not acid to litmus (**acids**).

Introduce into a glass-stoppered cylinder, which has been previously rinsed with sulphuric acid, 5 c.c. of liquid petrolatum and 5 c.c. of colourless sulphuric acid, heat in a water bath during 10 minutes, shaking well at intervals of 30 seconds; the oil remains unchanged in colour and the acid does not become darker than pale amber (**carbonisable impurities**).

Prepare a clear colourless saturated solution of lead oxide in an aqueous solution of sodium hydroxide (1 in 5) and mix 2 drops of this solution with 4 c.c. of liquid petrolatum and 2 c.c. of dehydrated alcohol; the mixture does not darken after heating for 10 minutes at 70° and cooling (**sulphur compounds**).

Viscosity.—Make a permanent mark about 2 cm. below the bulb of a 50 c.c. pipette of the usual type, and note the time in seconds required at 25° C. for the level of distilled water to fall from the upper to the lower mark as the liquid flows from the pipette. The time should not be less than 25 seconds, nor more than 30 seconds for the pipette selected. Draw the liquid petrolatum to be tested into this pipette, which should be clean and dry, and note the time in seconds required at 25° for its level to fall from the same upper to the lower mark as used for the water. Divide the number of seconds thus noted by the number of seconds required for water to fall from the upper to the lower mark as before determined. The quotient indicates the viscosity. Distilled water at 25° is taken as 1.

Ozokerite.—This substance, known also as cerasin, cerite, or mineral wax, usually occurs in the neighborhood of petroleum springs, and in association with bituminous sandstone, clay-schist, gypsum, and common salt. Though not very abundant, ozokerite occurs in many parts of the globe, the most remarkable and best-known deposit being that in the miocene rocks of Galicia, on the slopes of the Carpathian Mountains, and also on the Wallachian side of the range. It is also worked on the island of Tscheleken in the Caspian and at Swatoi-Astrow, near Aphesron, where a variety called *neftgil* is found. It exists also in Turkestan, and a valuable deposit has been found in Utah. Its commercial interest is chiefly as a source of cerasin, though liquid hydrocarbons are also obtained by the distillation of the inferior kinds.

According to Brannt ("Petroleum and Its Products," 400), Sauerlandt has found ozokerite to contain:

Volatile hydrocarbons.
Paraffins melting at from 60° to 70°.
Waxy resins, }
Bituminous resins, } Oxygenated.
Coke.

Crude ozokerite varies much in appearance. The finest varieties are transparent, of a pure yellow or greenish colour, and can easily be kneaded between the fingers. Crude Galician ozokerite is a scaly or waxy substance, with a resinous fracture. It is usually brittle, but as hard as beeswax. It becomes negatively electric by friction and exhales an aromatic odour. According to Lach (*Chem. Zeit.*, **13**, 831), the so-called ozokerite from Colorado does not yield cerasin, but is suitable for paraffin making. It begins to distil at 360°, and yields 90% paraffin and oil and about 5% of residuum. Caucasian ozokerite yields about 58% of a second-quality cerasin.

Inferior kinds of Galician ozokerite are black and soft, or hard, with a fibrous structure and conchoidal fracture, varying in colour from yellow ("butter-stone") to black. Some pieces are as hard as gypsum, and are dichroic, the transmitted light being a pure yellow, and the reflected dark green. The m. p. is very variable, ranging from 58° to 100°. The raw ozokerite occurring on the island of Tscheleken, in the Caspian Sea, is a brownish-black sticky mass, almost entirely soluble in boiling benzene. On extracting it with ether, the oily portion and colouring matter are dissolved, leaving a hard residue. On boiling this with acetic ether, the paraffin is dissolved, and by repeated treatment with animal charcoal, etc., may be obtained in lustrous crystals, melting constantly at 79°, and containing 85.10 of carbon and 14.57 of hydrogen (Beilstein and Wiegand, *J. Chem. Soc.*, **44**, 1073).

Ozokerite is separated from the gangue by being melted, and, after being pressed, is treated with alkali and filtered through fine animal charcoal. Frequently both acid and alkali are used in the purification of ozokerite; fuller's earth and magnesium silicate have been substituted for the charcoal. The charcoal used is preferably the fine carbonaceous residue produced in the manufacture of potassium ferrocyanide (cyanide black). The purification of ozokerite with sulphuric acid is attended with considerable loss, owing to the action of the acid on the oxygenated bodies present. Peritz obtained from 75 to 82% of crystallised paraffin from Boryslaw ozokerite, and 9 to 13% of light oils. Ozokerite refined in England yields nearly 70% of white paraffin. The purified substance constitutes *cerasin*, which name should be confined to the solid paraffin obtained without distillation. Inferior ozokerite is usually distilled with superheated steam, when it yields paraffin wax, lubricating oil, naphtha. Galician ozokerite yields, on distillation, about 25% of petroleum, 21 of lubricating oil, and 36 of solid paraffin. A higher yield might doubtless be obtained by improved manipulation. B. Redwood (*J. Soc. Arts*, xxxiv, 886) gives the products as 5% of gaseous hydrocarbons, 3% of naphtha, 6 of semi-solid "ozokerin," 12 of soft paraffin (melting at 44° to 46°), distilled ozokerite (melting at 61°), and a black waxy residue. The following are the products obtained by the distillation of Caspian ozokerite (*neft-gil*), according to Grabowski: 2 to 5% of benzine, 15 to 20% of naphtha, 15 to 20% of heavy oils, 36 to 50% of solid paraffin, and 10 to 20% of coke.

Sometimes the products are less carefully differentiated, the chief being:

30 to 40% of benzine of 0.73 sp. gr., and
50 to 76% of solid paraffin melting at from 60° to 70°.

The crude ozokerite is worked up for cerasin, paraffin being extracted from the residue, which then forms "ozokerite pitch." In distilling for paraffin, a burning oil comes over at 150°, the fraction 200°–300° consisting of a mixture of heavy oil and paraffin, and being worked up for the latter or for vaseline, while the chief yield of paraffin comes from the fraction 300°–350°. The average yield of the various distillation products is, at Boryslaw: Light oil (up to 150°), 6%; heavy oil (150°–300°), 32%; paraffin about 55%.

Analysis of Crude Ozokerite.—According to B. Lach (*Chem. Zeit.*, 1885, 905), for the valuation of crude ozokerite 100 grm. of the sample should be treated with 20 grm. of fuming sulphuric acid in a tared basin. The mixture is heated to 170° to 180°, and continuously stirred till all sulphur dioxide has escaped. On reweighing the basin, the loss is said to represent the volatile constituents—namely, ***petroleum*** and ***water***. No allowance appears to be made for the loss due to the formation of sulphur dioxide and possible volatilisation of sulphuric anhydride. Probably a better plan would be to dilute the mixture, and separate and weigh the paraffin. Lach further directs that another quantity of 100 grm. of the sample should be treated with 10 grm. of the carbonaceous residue from the manufacture of potassium ferrocyanide, which has been previously dried at 140°. A tenth part of the mixture (11 grm.) is then weighed into a tared paper thimble, and extracted with petroleum spirit, boiling between 60° and 80°. The wax is estimated from the loss, or recovered by evaporating the solvent. This result would probably be high, while the first method of Lach would undoubtedly be low; therefore it seems that the suggested modification of the first method would be the best to follow.

Refined ozokerite or cerasin usually melts between 61° and 78°, is quite odourless and colourless, and has a waxy section. A variety manufactured in Frankfort-on-the-Oder is said to melt at 83°, and to be so hard as scarcely to yield to the finger-nail. Cerasin possesses the general characters of paraffin wax. The commercial samples are sometimes artificially coloured.

Cerasin may be distinguished from bleached beeswax by its lower sp. gr. and by its resistance to alcoholic potash, no trace of saponifiable matter being present. In admixture with beeswax, cerasin may be detected and approximately estimated by the methods given in Vol. 2, page 90.

Ozokerite vaseline is obtained by allowing melted ozokerite to pass through 12 to 15 filters of animal charcoal, or through double that number if a perfectly colourless product be required. The mass is then treated, for 3 to 4 hours, with superheated steam (250°). About 25 to 30% of product is obtained.

PARAFFIN

Paraffin Wax. Solid Paraffin

Paraffin is found native in the coal measures and other bituminous strata, constituting the minerals known as fossil wax, hatchettin, ozokerite, etc. It exists also in solution in many kinds of petroleum, and is obtainable therefrom by distilling off the more volatile portions and exposing the remainder to a low temperature. Solid paraffin may be obtained in a similar manner from the tars of wood, cannel coal, and bituminous shale, and is now manufactured on an enormous scale from the last source.

Paraffin is a white or bluish-white, waxy solid, without taste or smell. Its density and m. p. vary with its composition, and the same is true of its b. p., which is very high. Exposure to continued heat, aided by pressure, resolves paraffin into liquid hydrocarbons, and the same result is partially obtained by distillation. By merely raising the temperature to 370° it undergoes decomposition, with separation of carbon and formation of permanent gas, liquid products, and a paraffin of lower m. p. It contains about 85% of carbon and 15% of hydrogen.

The sp. gr. of paraffin increases with its m. p., as is shown by the following results attained by Galletly from Boghead coal product:

Sp. gr.	M. p.	
0.8236	32.0° C.	89.6° F.
0.8480	39.0° C.	102.2° F.
0.8520	40.5° C.	104.9° F.
0.9090	153.3° C.	128.0° F.
0.9110	153.3° C.	128.0° F.
0.9243	58.0° C.	136.4° F.
0.9248	59.0° C.	138.2° F.
0.9400	80.0° C.	176.0° F.

G. Beilby (*J. Chem. Soc.*, **43**, 388) has given the following data respecting the sp. gr. of a sample of shale-oil paraffin melting at 38°.

	Sp. gr.
In the solid state, at 21°	0.8740
Dissolved in 0.885 paraffin oil, at 21°	0.7950
In the melted state (calculated at 21°)	0.7956

From this it appears that paraffin in solution has practically the same density as when in the melted state.

The data in the following table, obtained in Allen's laboratory, show the relations between the solidifying-point of paraffin wax and its density in the solid and liquid state. The determinations of sp. gr. of solid samples were in most cases made as described, but, on repetition, the figures obtained were not very concordant. The density at 99° was determined by the plummet, and the solidifying-point was ascertained by Dalican's Method, Vol. 2, page 73.

Origin of sample	Sp. gr.		Solidifying-point,°
	Solid, at 15.5°	Liquid, at 99°	
1. Shale oil	0.8666	0.7481	44.0
2. Shale oil	0.8961	0.7494	47.0
3. Shale oil	0 9000	0.7517	52.0
4. Shale oil	0.9111	0.7572	58.5
5. American petroleum	0.9083	0.7535	53.8
6. Ozokerite	.....	0.7531	61.5
7. Rangoon tar	0 8831	0.7571	49.0

From these figures it appears that, except in the case of the refined ozokerite, there is a regular increase in the sp. gr. with a rise in the m. p., as was observed by Galletly. There is a striking contrast between the densities of the waxes in the melted state at 99° and the densities of the same samples when solid, the range in the latter case being, for the shale products, 5 times as great as in the former. In other words, the density of paraffin wax is far more constant when melted than in the solid state. It also appears that paraffin is much less dense in the melted state than the oil from which it crystallises on cooling, a sample of which had a sp. gr. of 0.843 at 99°. Vaseline also is considerably denser than paraffin.

Paraffin melting from 32° to 43° exhibits a well-defined crystalline fracture; from 43° to 50° the crystals become much smaller and less marked, and from 50° upward the fracture is very close and fine in the grain. Paraffin that melts at 65° presents, on fracture, brilliant, white, acicular crystals having a silky lustre, and that melting at 77° closely resembles bleached beeswax, but the fracture is not conchoidal.

When paraffin is kept for some time under gentle pressure, the temperature being somewhat below its m. p., a molecular change occurs, and the substance becomes transparent. A sudden change of temperature or a sharp blow or knock causes the mass to return to its original state, but it may be annealed by slow cooling.

Paraffin becomes plastic at a temperature considerably below its m. p., a fact which is disadvantageous when it is employed for making candles, but which is to a great extent obviated by a small admixture of stearic acid, wax, or other foreign substance.

Mixtures of paraffins of different fusing-points melt at a temperature which is the mean of the m. p. of the constituent hydrocarbons; but the products obtained by melting together paraffin wax and stearic or palmitic acid, beeswax, etc., always have a m. p. *lower* than the mean of those of their constituents. This is well shown by the following table from Vincent's *Manufacturing Chemistry*, the results recorded being obtained from mixtures of the Musselburgh Company's stearic acid, melting at 130° F., with various proportions of 3 varieties of Young's paraffin:

Stearic acid	Paraffin	M. p. of mixture. Paraffin melting at		
		48.8°	52.2°	52.7°
55	45	45.5	45.3	46.4
60	40	48.3	46.6	47.7
65	35	49.4	47.7	48.8
70	30	50.3	50.3	50.3
75	25	51.4	51.1	51.1
80	20	52.0	52.0	52.0
85	15	52.2	52.7	52.7
90	10	53.0	53.3	54.1
95	5	53.6	53.8	54.4

When 2 pieces of paraffin are sharply struck together, a metallic ring is heard, the sound being sharper the higher the m. p. of the paraffin.

Paraffin is completely insoluble both in hot and cold water. It is insoluble in rectified spirit, and but sparingly soluble in boiling absolute alcohol, the dissolved portion separating again on cooling. It is moderately soluble in petroleum spirit, shale naphtha, kerosene, ether and benzene, essential oils, and fixed oils. It is rather more soluble in toluene than benzene, and in xylene than in toluene. Hence it is miscible with all kinds of vegetable and animal oils and fats. It differs from these in its indifference to alkalies, and cannot be saponified. If, however, the soap be made from a mixture containing carnauba wax as well as paraffin, the latter is completely dissolved by the alkali, a fact which is said to be attributable to its solubility in the myricyl alcohol, $C_{30}H_{61}OH$, which is a constituent of the carnauba wax.

Paraffin burns with a very bright but not smoky flame, and hence is much employed for making candles and tapers. *Paraffin candles* usually contain from 5 to 15% of stearic acid. The presence of the admixture may be detected by adding a little powdered fuchsine to the sample and keeping it at 100° for some time. If pure, the melted paraffin will remain uncoloured, but with 2% of stearic acid a pink colour is produced, and if as much as 5% be present, the whole mass becomes crimson. Coloured candles are made by dissolving the fuschine or other colouring matter in stearic acid or beeswax, and adding the product to the paraffin until the desired tint is obtained.

Boiled with concentrated nitric acid, paraffin is oxidised, with formation of various products, of which the most characteristic are succinic acid, $C_4H_6O_5$, and cerotic acid, $C_{27}H_{54}O_2$, the production of the latter of which points to the presence of the hydrocarbon, $C_{27}H_{56}$, in the original substance. Cerotic acid was also the chief product obtained by Gill and Meusel by the oxidation of a paraffin, melting at 56°, by means of chromic acid mixture.

Paraffin is also violently oxidised by permanganate of potassium mixed with sulphuric acid and heated. Concentrated sulphuric acid attacks it at high temperatures, and the more readily the higher the m. p. of the sample.

When heated with sulphur, paraffin is decomposed, with evolution of hydrogen sulphide and separation of carbon.

For the quantitative analysis of mixtures of paraffin with *fatty acids* or *fats*, the process described in Vol. 2, page 549, is suitable. The detection and estimation of paraffin in *beeswax* can be effected as described in Vol. 2, pages 335 and 337.

Paraffin Scale. *Crude Paraffin.*—"Scale" is the technical name for the crude paraffin deposited by cooling the oils holding it in solution. The lower the temperature employed for refrigeration, the lower the m. p. of the paraffin deposited.

In the practical analysis of paraffin scale, methods must be employed which are acceptable under reasonable conditions by all interested parties. The following are the methods adopted by the Scottish Mineral Oil Association and certain representative purchasers:[1]

Sampling.—The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

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[1] *J. Soc. Chem. Ind.*, 1891, 342.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, wagon, or bing.

Preservation of Samples.—Immediately after the sample has been drawn, it is to be thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

Estimation of Oil. (*a*) *Press.*—No special form of press is recommended for general adoption, but it must have some arrangement for indicating the pressure applied. The cup in which the scale is placed during the application of pressure should have an area of 20 sq. in.

(*b*) *Preparation of Sample.*—A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool overnight to a temperature of 15.5°. The solid mass is then ground to a fine powder, a portion of which is used in the estimation of the oil.

(*c*) *Quantity and Conditions.*—The quantity of scale to be used in the estimation of oil is to be 250 (12.7 grm.) grains, which may, however, be reduced to 150 (7.6 grm.) grains in the event of the scale containing much oil (over 7%). With "soft" scale the smaller quantity should be taken.

(*d*) The temperature of the scale and the press is to be 15.5°.

(*e*) The scale is to remain under pressure for 15 minutes.

(*f*) Fine linen pressing cloths and a number of layers of filter-paper sufficient to absorb all the oil are to be used. The exterior papers must not be soiled by oil.

(*g*) The maximum pressure is to be 10 cwt. per sq. in., and the working pressure 9 cwt. per sq. in.

Estimation of Water.—The amount of water present in paraffin-scale may be estimated by either of the following processes:

(*a*) *Distillation from a Copper Flask.*—From 1 to 2 pounds of the scale are heated in a conical copper flask of about the following dimensions: 27.5 cm. (11 in.) high over all, 20 cm. (8 in.) diameter at the base, and 0.4 cm. (1.5 in.) at the neck. The bottom of the flask is slightly concave downward. This is connected with an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with hydrated gasoline or naphtha and added to the principal quantity.

(*b*) *Price's Company's Method.*—500 (25.3 grm.) grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 110°, until bubbles cease to be given off; the loss is then determined.

500 (25.3 grm.) grains of the *same scale*, which has been freed of its water and dirt by melting at a gentle heat and subsidence, are to be heated in the same way to a similar temperature for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment; the remainder is taken as the quantity of water present.

Estimation of Dirt.—The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale, and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha, thrown on a weighed dry filter-paper, washed with naphtha or gasoline, dried, and weighed. When available, the quantity of scale to be used in the estimation of the percentage of dirt should not be less than 1 pound.

Calculation of Results.—As the oil is estimated in scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

Determination of the Melting (Setting) Point of Solid Paraffin.—This may be determined by what is known as the "English" test; *i. e.*, a test-tube about 1 in. in diameter is filled to the depth of about 2 in. with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

The Saybolt apparatus, using metal boxes placed on a support which is moved back and forth with thermometers immersed in the melted paraffin contained in the boxes, is a modification of the English method.

What is technically known in England as the "m. p." of paraffin scale is in reality the solidifying-point, and can be ascertained by Dalican's method, Vol. 2, page 73.

Boverton Redwood (*J. Soc. Chem. Ind.*, 1884, 3, 430) has devised a special machine for testing paraffin scale, and the greater part of that imported from America is sold on the results of the analysis by Redwood's test. The apparatus consists of a press furnished with a gauge for indicating the pressure applied. The test is, of course, a purely arbitrary one, depending upon (*a*) temperature, (*b*) amount of pressure applied, (*c*) length of time during which the pressure is continued, and (*d*) quantity of scale operated upon in relation to the diameter of the press-cake. The operation is conducted at 15.5, which temperature must be closely adhered to. The quantity of scale operated upon is 500 grains, and the pressure is applied for 5 minutes. The gauge of the press indicates from 1 to 10 tons, and the working pressure is 9 tons on the whole surface of the press cake of 5⅝ in. diameter, equal to about 7 cwt. per square in. The sample is placed between 2 circular pieces of filter-cloth in a turned iron cup into which the ram of the press fits, and a sufficient number of circular pieces of filtering paper are placed above and beneath the cloth to absorb the expressed oil. The press cake is carefully removed from the cloth at the expiration of 5 minutes, and the loss in weight noted. The proportion of oil in American scale usually ranges between 1 and 12%. Much depends upon the proper drawing and averaging of the samples of scale. A good plan is to sample one cask in 20 by taking out a core with a sampling iron driven into the centre of the cask, and then mix the sample by passing it through a small hand sausage-machine.

In the United States the paraffin scale is melted over a water-bath in a hemispherical tinned iron or glass dish, 3 or 4 in. in diameter. The dish is then placed on a stand where slow cooling can take place, in a room at a temperature of about 15.5°, and a thermometer, with a spherical bulb ½ in. in diameter, is suspended over the centre of the dish so that ⅞ of the bulb is immersed in the paraffin. The surface of the melted scale is then carefully watched, and the temperature noted at which a "spider" extends from the edge of the liquid to the bulb of the thermometer. The "spider" or network makes its appearance before there is any uniform film over the surface, and is not readily observable unless the observer be suitably placed in relation to the source of light. Redwood, to whose published papers and private communications Allen was indebted for much information on the subject of petroleum-products, states that the results of the American test are from 2.5° to 3.0° F. higher than those obtained by the English test.

The following methods are improvements over the English method:

The solidifying-point is best determined by the method of Shukoff. 30–40 grm. of the paraffin is melted in a narrow flask inserted by means of a rubber stopper in a bottle, the same as is used for the solidifying-points of fats (so-called "titer test").

As soon as the temperature of the mass stated has dropped to about 5° above the solidifying point, the apparatus is strongly and regularly shaken until the contents is distinctly turbid. Then, without further shaking, one observes the point at which the thermometer remains constant and then rises. The highest point then reached is the solidifying-point of the paraffin.

Dr. Rich Kissling (*Rev. Fett Harz. Ind.*, **15**, 46–9) modifies the method slightly by suggesting the use of a Dewar bulb, which is filled with melted paraffin to within 10 mm. of the upper edge. It is suspended in a water-bath, the temperature of which is about 5° above the solidifying-point of the sample. When the temperature of the bulb and the bath are the same, the bulb is shaken until the paraffin foams, when it is allowed to rest. This paraffin is still clear, but close to the point of turbidity. The temperature is read from the thermometer in the bulb until it remains constant from 3 to 6 minutes.

True Paraffin.—Paraffin stock is tested for its content of true paraffin scale, according to Holde, as follows: 0.5 to 1.0 grm. of the substance is dissolved in a wide test-tube in ethyl ether, avoiding an excess of ether. A volume of absolute alcohol, equal to the ether used is added and filtered by means of suction in a funnel surrounded by a freezing mixture of ice and salt at a temperature of -20 to $-21°$. It is washed with a mixture of equal volumes of ether and absolute alcohol chilled likewise by immersion in a freezing mixture. After washing, the paraffin is dissolved with hot benzene into a weighed flask and paraffin estimated by weighing after the evaporation of the benzene.

ASPHALT

Asphaltum. Mineral Pitch

German—Erdpech. *French*—Asphalte. *Spanish*—Asfalto.

Under the term asphalt is included broadly a considerable number of natural products, consisting largely of compounds of carbon and hydrogen mixed with substances containing oxygen, nitrogen, and sulphur, also some mineral matter.

Prof. S. F. Peckham describes asphalt as follows: "the natural bitumen, which is known as asphalt, is composed, as far as we have been able to learn, of unsaturated hydrocarbons and their sulphur derivatives with a small amount of nitrogenous constituents. Asphalt may, therefore, be defined as any hard bitumen composed of unsaturated hydrocarbons and their derivatives, which melts on the application of heat to a viscous liquid; while a maltha or soft asphalt may be defined as a soft bitumen which, on heating, leaves an asphalt, or becomes by natural causes converted into one. The line between the two classes cannot be sharply drawn.

"Asphalts are distinguished by the large amount of sulphur they contain, and it is to its presence that many of the important characteristics and perhaps, in part, the origin of this form of bitumen is due. The soft asphalts or malthas contain much less sulphur than the harder ones, if the former are rich in sulphur, they are then in a transition stage and would eventually become hard."

Before proceeding to discuss asphalts in the narrower sense it is desirable to distinguish two classes of solid bituminous products that are closely related and therefore are sometimes confused with true asphalts.

We refer to the **asphaltites** or natural asphalt-like substances characterized by high fusing points (over 250° F.) and including Gilsonite of Uintaite, Glance Pitch or Manjak, and Grahamite, and the **Asphaltic Pyrobitumens,** including Elaterite, Wurtzilite, Albertite, and Impsonite, which are infusible without decomposition.

Gilsonite, found only in Uinta Co., Utah is widely used in the manufacture of so-called asphalt paints and varnishes and as a tempering or hardening agent in mixing with soft asphalts. It is also miscible in all proportions with fatty acid pitches and is used extensively in compounding artificial wax mixtures.

Glance Pitch (Chapapote, Manjak, Syrian Pitch) is similar to Gilsonite but with black streak on porcelain instead of brown as with Gilsonite. It has a higher sp. gr. than Gilsonite and a lustrous conchoidal fracture. It is used largely for varnishes and similar uses.

Grahamite was first found in West Virginia. It is also obtained from Oklahoma, Mexico, Trinidad and elsewhere. It is of higher sp. gr. than gilsonite or glance pitch and is of somewhat crumbling fracture. Its fusing point is 350° F. and higher. When free from mineral matter it is practically all soluble in carbon disulphide and blends with residual oils and soft asphalts.

The **Asphaltic pyrobitumens.** Abraham (*Asphalts and Allied Substances*, 1918, p. 149) considers that "all four of this class are derived from the metamorphosis of petroleum, and it is probable that the impsonite represents the final step of transformation of elatorite, wurtzilite and albertite, as well as the asphaltites (gilsonite, glance pitch and grahamite").

Wurtzilite, although infusible without decomposition in its natural state and only slightly soluble in petroleum naphtha, by heating to about 500° F. in a closed vessel under pressure, is changed in character, becoming fusible and readily soluble in carbon disulphide and moderately so in 88° naphtha. It is used in the manufacture of asphalt paints and varnishes.

Albertite, found in 1849 in New Brunswick, was mainly used to enrich bituminous coal in the manufacture of illuminating gas. While this or analogous materials have been found elsewhere, the New Brunswick occurrence is the one best known and it is now exhausted.

Deposits of asphalt occur in all parts of the world; each locality yields a material more or less distinct in character. Much attention has been paid to the analysis of asphalt, especially in the United States, owing to the discovery of new and important local deposits and the extensive introduction of asphalt-paving in American cities. This paving is often merely an asphaltic mixture, inferior to the rock-asphalt employed in Europe. Even mixtures of coal-tar pitch, and petroleum residuum without true asphalt have been used.

Natural asphalts exhibit wide differences in composition. Some forms (rock-asphalts) consist of limestones or sandstones saturated with bituminous matter. In other cases but little mineral matter is present, and in still other cases the mineral matter is abundant, but is simply mixed with the bituminous material and does not produce a rock-asphalt.

Blake (*Trans. Amer. Inst. Min. Eng.*, 1889–90, 563) gives the following list of the principal localities of the several types of asphalt:

Mixed with calcium carbonate	Seyssel; Val de Travers; Lobsann; Illinois.
Mixed with sandstone	California; Kentucky; Utah.
Mixed with earthy matter (clay).	Trinidad; Venezuela; Cuba; California; Utah.
Bituminous schists	Canada; Kentucky; California; West Virginia.

Still more important deposits of oil shales, closely analogous to the bituminous schists, have been located, and are being developed experimentally, in western Colorado and eastern Utah.

Some asphalts, such as Trinidad and Bermudez, are submitted to a refining process before being marketed. This consists in heating the crude material in large kettles to not over 200°, by which much water and some volatile matters are removed, portions of the earthy materials, principally clay and sand, allowed to settle, and some of the non-bituminous organic substances collect as a scum and may be removed. Petroleum residuum may be added during this operation, which will, of course, increase the amount of bituminous matter, especially that soluble in petroleum spirit, and produce a strongly fluorescent solution.

Although asphalts have been used for a long period in engineering work, the first scientific investigation seems to have been made by Boussingault (*Ann. d. Chim.*, 1837, **64**, 141; also *Compt. rend.*, Meeting of Sept. 16, 1836), who, in 1836, examined a viscous material from Pechelbronn. He tried several solvents, but relied more upon a process of distillation in an oil-bath, by which he obtained a liquid to which he gave the name "pétrolène." He assigned to this a composition of $C_{80}H_{64}$ ($C = 6$), pointing out that it was isomeric with oil of turpentine. The non-volatile portion he designated "asphaltène," and assigned to it the formula $C_{80}H_{64}O_6$ ($C = 6$, $O = 8$), but recognised that oxidation had occurred during the distillation, and that therefore the proportion of asphaltène obtained was in excess of the true amount. From an ultimate analysis of the material, he computed that the proportions of pétrolène and asphaltène were about 85.4 and 14.8, respectively. He also made a brief examination of the asphalt of Coxitambo.

Boussingault's methods are not now used, but by a curious misapplication, the terms petrolene and asphaltene have been applied to the products obtained by the use of solvents. Efforts have been made to establish standards for judging of the value of an asphalt for engineering uses by means of these methods. Carbon disulphide is sometimes used to determine the total bitumen, all organic matter left undissolved being regarded as non-bituminous. For the fractionation of the bituminous matter, petroleum spirit, ethyl ether, acetone, boiling oil of turpentine, chloroform, and benzene have been employed. Usually the portion soluble in petroleum spirit, ether, or acetone is called petrolene, and that insoluble in either of these liquids, but dissolved by boiling turpentine and cold chloroform, is designated as asphaltene. The organic matter insoluble in any of these solvents, and also in carbon disulphide, is considered as non-bituminous, and is thought to be objectionable if present in notable proportion, rendering the paving mixtures liable to rot in the gutters. On the other hand, a large per cent of fine colloidal clay may be present and as Clifford Richardson has maintained may constitute a valuable element in the asphalt mixtures made from Trinidad Lake asphalt. Many engineers have adopted or accepted limits of the proportion of petrolene to asphaltene in asphalts intended for paving purposes. Thus, Tillson (Trans. Amer. Soc. Civ. Eng., 1897, 214) accepts any refined asphalt that contains from 50 to 60% of bitumen of which not more than 25 to 30% is asphaltene. This does not apply to rock-asphalts, which may contain less than 10% of bitumen. Petrolene is regarded as acting as a solvent on the asphaltene.

The calcareous asphalts have a deep brown or black colour, and break without any sign of cleavage, the fracture being earthy and very similar to chocolate both in colour and appearance. When long exposed to the air, the surface acquires the appearance of ordinary limestone, but on fracturing the specimen the interior will be found unchanged. The proportion of bitumen cannot be judged from the appearance.

The average sp. gr. of rock-asphalt is about 2.23. It is very hard and sonorous when cold, and may be broken with a hammer. In summer it is softened by blows to a kind of paste, and at 50° to 60° falls to powder. Some rock-asphalts, such as that of Lobsann, contain a volatile oil which renders them greasy. This oil may be removed by distillation, after which the asphalt is fit for use.

Good rock-asphalt has a fine and homogeneous grain, and no particle of white limestone is visible. The rock is often streaked, while other samples contain crystals of calcite of considerable size, but impregnated with bitumen like the matrix, which is an important characteristic. Bad qualities are imperfectly impregnated, or contain so small a proportion of bitumen as to render it difficult to work them. The presence of clay spoils the homogeneous nature of the asphalt, and causes fissures.

When intended to be used for paving, the Val de Travers, Seyssel, and other rock-asphalts are often melted with a certain proportion of rich native asphalt, such as Trinidad pitch, the product being called "mastic." The mastic is often mixed with a further proportion of bitumen, residuum, shale oil, and mineral matter.

Composition of Rock-asphalts.—The following data are compiled from various sources, as indicated. The detailed statement of the mineral ingredients is given somewhat vaguely in some of the reports, but the principal ingredients will serve for comparison. The loss at or about 100° is designated by some analysts as water, but it may include bituminous matters:

Source	Loss at 90°	Soluble in carbon disulphide	Calcium carbonate	Magnesium carbonate	Sand or clay	Sulphur	Authority
Ragusa		9.72	88.75				Tillson.[1]
Seyssel		8.15	91.70				Tillson.[1]
Seyssel	190	8.00	89.55	0.10	0.25		Orton.[2]
Val de Travers		7.20					Tillson.[1]
Val de Travers		12.00					Tillson.[1]
Val de Travers	0.50	10.10	87.95	0.30			Orton.[2]
Limmer		14.30	67.00		17.52		Sadtler.[3]
Limmer		8.26	56.50	27.01	4.98		Orton.[2]
Vorwohle		5.37	90.80		2.55		Sadtler.[3]
Lobsann	3.40	11.90	69.00	0.30	3.05	5.00[6]	Orton.[1]
Forens	0.20	2.25	97.00	0.70			Orton.[1]
California	2.50	20.20	3.00		74.00		Hilgard.[4]
California	0.33	15.13			83.40[7]		Linton.[5]
Kentucky		5.76			94.22[7]		Linton.[5]
Turrelite (Texas)		12.05	87.94[7]				Linton.[5]

[1] Trans. Amer. Soc. Civ. Engin., 1897. [2] Rep. to Geol. Survey of Ky. (data from German sources). [3] *Ind. Org. Chem.* [4] Ann. Rep. State Mineral. of Calif., 1890; average of fourteen samples. [5] *J. A. C. S.*, 1894 and 1896. [6] Present as iron sulphide. [7] Total mineral matter; the details of composition are not given, except that Turrelite is stated to consist largely of sea-shells cemented into a mass by the bitumen.

Composition of Soft Asphalts.—The natural asphalts, other than the true rock-asphalts, show great differences in composition, both as regards the proximate constituents and the nature and amount of mineral matter. The following table includes the more important forms. The total bituminous matter has usually been estimated by solution in carbon disulphide, or by successive extraction with petroleum spirit, boiling turpentine, and chloroform. The mineral matter is mostly a ferruginous clay. The ash, obtained by burning a known weight of the asphalt, does not represent exactly the mineral matter in the original material, but the difference is not important, as at present the details of its composition have no practical value. A group of analyses of Trinidad asphalt are here given as reported by Clifford Richardson (*J. Soc. Chem. Ind.*, 1898, **17**, 13).

CRUDE LAKE PITCH

	Percentage soluble in			Percentage of total bitumen only soluble in			
	Petroleum spirit	Boiling spirits turpentine	Chloroform	Total bitumen	Petroleum spirit	Boiling spirits turpentine	Chloroform
Average	35.2	12.4	5.2	52.8	66.8	23.3	9.9

CRUDE LAND PITCH

Average	33.3	11.9	6.5	51.7	64.7	23.0	12.3

AVERAGE COMPOSITION OF TRINIDAD LAKE PITCH FROM THE BORING

54.66	35.90	9.44	31.53	57.67

AVERAGE COMPOSITION OF LAKE PITCH, DRIED (IN VACUO), KEARNEY COLLECTION

	Bitumen-soluble CS_2, %	Mineral matter, %	Organic, not soluble, %	Bitumen-soluble petroleum naphtha, %	Total bitumen-soluble, %
Average	54.25	36.51	9.24	35.41	65.27

AVERAGE COMPOSITION OF LAND PITCH, DRIED (IN VACUO), KEARNEY COLLECTION

EIGHT SPECIMENS FROM LOT C., NEAR THE LAKE

	Bitumen-soluble CS_2, %	Mineral matter, %	Organic, not soluble, %	Bitumen-soluble petroleum naphtha, %	Total bitumen-soluble, %
Average..........	54.03	36.49	9.48	33.02	61.11

FOUR SPECIMENS FROM CROWN LAND LOTS ADJOINING C.

Average..........	58.81	36.62	9.57	32.29	60.01

COMPARATIVE COMPOSITION OF 1894 SAMPLES

	Bitumen	Organic insoluble	Mineral inorganic
Lake, 2 ft. below surface............	54.92	9.72	35.46
Land............................	52.36	11.24	36.40

	Bitumen soluble in naphtha	Total bitumen soluble in naphtha
Lake, 2 ft. below surface............	31.72	57.79
Land............................	29.02	55.43

Adulterations of Asphalt and Asphaltic Mixtures.—Pure asphalt is much employed in the manufacture of black varnishes and japans and for other similar purposes. It is not infrequently mixed with or substituted by *coal-tar pitch* and other artificial products, which render it quite unfit for some of its most important uses.

Asphalt for varnish-making should be entirely (or with the exception of 4 or 5% of earthy matters) soluble in carbon disulphide, chloroform, high-boiling coal-tar naphtha, and oil of turpentine. It is also said to be insoluble in alcohol or a mixture of equal parts of alcohol and chloroform. It should break with a conchoidal fracture and brilliant resinous lustre, the streak and powder being of a bright brown. Asphalt should not flow or lose shape like wood-tar pitch when left on a plane surface, and an angular fragment or chip should retain its shape and the sharpness of its angles in boiling water, and only begin to melt at about 150°. Asphalt adulterated with coal-tar pitch has a much less brilliant fracture-surface, and an adamantine or metallic rather than a resinous lustre. When fused at as low a temperature as possible, the adulterated asphalt has a granular pasty appearance and feel, instead of being smooth and homogeneous, and will not draw out into even and transparent brown threads like pure asphalt.[1]

The following figures, due to E. Davies (*Pharm. J.* [3], 14, 394), show the behaviour of certain natural asphalts, rock-asphalts, and their substitutes, with petroleum spirit. The proportions of sulphur and mineral matter are also recorded.

For these analyses, 5 grm. of the finely-divided sample were digested for 1 hour with 50 c.c. of petroleum spirit of 0.70 sp. gr., and the mixture frequently agitated. The liquid was then boiled for a short time, decanted, and the residue boiled with another quantity of 25 c.c. of petroleum spirit. This treatment was repeated 8 or 10 times, till the exhaustion was complete.

Material	Ash	Action of petroleum spirit		Proportion soluble for 100 of organic matter	Sulphur	
		Soluble	Insoluble		Per 100 of material	Per 100 of organic matter
Val de Travers asphalt	90.24	9.76	none	100.00	0.41	4.20
Fine Syrian asphalt	0.68	48.16	51.16	48.49	6.13	6.19
Low Syrian asphalt	2.64	49.68	47.68	51.02	5.65	5.80
Trinidad pitch	37.76	36.24	26.00	58.22	3.47	5.58
—	—	—	—	—	—	—
American asphalt	0.60	65.64	33.70	66.03	0.62	....
American asphalt	0.26	63.62	36.12	63.78	0.85	....
Stearin pitch	5.50	71.05	23.45	75.18	0.04	....
Stockholm pitch	0.84	91.46	7.70	92.23	0.01	....
Rosin pitch	0.58	86.94	12.48	87.45	0.26	....
Coal-tar-pitch	0.20	24.44	75.36	24.29	0.69	....
Coal-tar pitch	1.06	18.70	80.74	18.90	0.41	....
Coal-tar pitch	0.48	15.86	83.66	15.94	0.59	....

Of these samples, those called "American asphalt" were evidently manufactured and not natural products. They were probably petroleum pitch, and were black, brittle substances, having a conchoidal fracture and black streak. They differed from stearin pitch in their brittleness and the proportion of sulphur. The Stockholm pitch was black, too soft to powder, and very easily soluble in petroleum spirit. The rosin pitch had a conchoidal fracture, and gave a brown powder. The different proportions of matter soluble in petroleum spirit present in the samples of coal-tar pitch were, no doubt, due to the extent to which the respective distillations had been carried.

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[1] The characters of asphalt fitted for varnish-making given in the text are taken from Spon's *Encyclopædia*. They apply to refined asphalt.

For the distinction between natural asphalt and coal-tar pitch reliance has sometimes been placed on the fluorescence of the petroleum-spirit solution when coal-tar products are present, but some crude asphalts also produce fluorescence, and refined asphalt may contain petroleum residuum. Durand-Claye suggested the following test: the sample is digested in carbon disulphide, filtered, the filtrate evaporated to dryness, and the residue heated until it is hard and brittle after cooling: about 0.1 grm. is shaken for a few minutes with 5 c.c. of fuming sulphuric acid in a stoppered tube, the mixture allowed to stand for 24 hours, and then 10 c.c. of water added, drop by drop, with constant stirring, after which the liquid is filtered through paper. Natural bitumens will give a colourless or faintly coloured solution, but coal-tar pitch will give a dark brown. If the conditions of the test are uniform, approximate quantitative comparison of samples may be made. The following comparisons were made in Allen's laboratory:

Rock asphalt	Faintly colored.
Trinidad asphalt	Slight brown.
Petroleum pitch	No color.
Shale-oil pitch	Hair brown.
Coal-tar pitch	Very dark brown.
Bone pitch	Very dark brown.

According to Durand-Claye, 8 grm. of the sample are shaken with 5 c.c. of benzine in a closed glass vessel until dissolved. A few drops of the filtered solution are then diluted with 5 c.c. benzine and mixed with an equal volume of alcohol (85°, Gay-Lussac). The yellow or yellowish-brown coloration of the alcoholic layer gives an indication of the presence of tar distillation products. Even on dissolving in benzine some indication can be obtained, since native asphalt dissolves with a pure brown colour, whilst tar products give a strongly yellowish-green fluorescence.

To detect the presence of coal-tar pitch in asphalt, a small amount may be heated in a crucible. In this way coal-tar pitch may be distinguished from natural asphalt by its disagreeable, bituminous odour. Another very definite test for coal-tar pitch is due to the fact that it always contains free carbon in contradistinction to asphalt. Natural asphalts present a uniform brownish appearance when a very little is melted on a hot microscope slide and examined under a microscope. The free carbon in coal-tar pitch may be seen suspended in the bituminous matter that otherwise would look much like the asphalt.

Asphalt-paving Mixtures.—Many asphalts are unsuited for use in street-paving unless mixed with tempering materials. Practice, in American cities especially, has led to the selection of special proportions of petroleum residuum, sand, or stone-dust, and pulverised limestone. As a guide to the composition of these mixtures the official specifications of two large cities and some engineering notes are given. The Philadelphia specifications are in part based on the results of an examination made some years ago (Report of experts (Sadtler, Leffmann, and Lewis) selected by Citizen's Municipal Association and the Trades' League of Philadelphia, 1894), but agree in the main with those of most American cities.

Philadelphia, 1894.—"If natural rock-asphalt is used for the wearing surface, it shall be natural bituminous limestone rock. From the Silician mines at Ragusa of the Catania mines, equal in quality and composition to that mined by the United Limmer and Vorwohle Rock Asphalt Company, Limited. From the Swiss mines of Val de Travers, equal in quality and composition to that mined by the Neufchatel Rock Asphalt Company, Limited. From the French mines at Seyssel, equal in quality and composition to that mined by Compagnie Générale des Asphalte de France in the proportions of 4 parts of the Sicilian Rock to 1 of the Seyssel or Vorwohle Rock.

"If refined asphalt is used for the wearing surface, it shall be composed of the best quality of refined Trinidad or Bermudez asphalt, obtained from the so-called pitch or asphalt lake on the Island of Trinidad or from Bermudez, South America, or other asphalt which in quality and durability shall be equal to the standard of the Lake Trinidad or Bermudez, heavy petroleum residuum oil, fine sand, fine stone-dust, fine powder of calcium carbonate. The asphalt must be refined and, as far as possible, freed from organic and mineral matter and volatile oil, and should contain at least 60% of bituminous matter soluble in carbon disulphide; the residuum oil must be free from coke and other impurities, of a sp. gr. of 18 or 22 Baumé, and withstand a fire test of 250° F. The refined asphalt and residuum oil will be mixed in the following proportions by weight: asphalt 100, petroleum 16 to 22.

"The asphaltic cement, made in the manner above described, will be mixed with other materials in the following proportion by weight, *viz.*:

"Asphaltic cement	13 to 16
Sand	58 to 63
Stone-dust	23 to 28
Pulverised limestone	5 to 3"

Complete specifications for making asphalt pavements including the foundations are rather lengthy, and the scope of this work only permits including the asphaltic layers themselves. Very full treatment of the entire subject can be obtained from a report of the commissioners of Account of the City of New York on Asphalt Paving, Feb. 3, 1904, and by consulting "The Modern Asphalt Pavement," by Clifford Richardson, New York, 1905.

Analytical Methods for Asphalts

The methods first given are the official methods of the Society for Testing Materials (U. S. A.), and, as far as they go, are standard. Many additional tests are given by Clifford Richardson, and his methods are given in full, even duplicating in some measure those of the Society.

Drying the Sample and Preparing It for Analysis.—It was decided, owing to the great variety of conditions met with in bituminous compounds, that it is impossible to specify any one method of drying that would be satisfactory in every case. It is, therefore, supposed that the material for analysis has been previously dried, either in the laboratory or in the process of refining or manufacture, and that water, if present, exists only as moisture in the hygroscopic form.

The material to be analysed, if hard and brittle, is ground and spread in a thin layer in a suitable dish (iron or nickel will answer every purpose) and kept at a temperature of 125° for 1 hour. In the case of paving mixtures and road materials, where it is not desirable to crush the rock or sand grains, a lump may be placed in the drying oven until it is thoroughly heated through, when it can be crushed down into a thin layer and dried as above. If the material under examination contains any hydrocarbons at all volatile at this temperature, it will of course be necessary to resort to other means of drying.

Analysis of Sample.—After drying, from 2 to 15 grm. (depending on the richness in bitumen of the substance) are weighed into a 150 c.c. Erlenmeyer flask, the tare of which has been previously ascertained, and treated with 100 c.c. of carbon disulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside and not disturbed for 48 hours. The solution is then decanted off into a similar flask, that has been previously weighed, as much of the solvent being poured off as possible without disturbing the residue. The first flask is again treated with fresh carbon disulphide and shaken as before, when it is put away with the second flask and not disturbed for 48 hours.

At the end of this time the contents of the 2 flasks are carefully decanted off upon a weighed Gooch crucible fitted with an asbestos filter, the contents of the second flask being passed through the filter first. The asbestos filter shall be made of ignited long-fibre amphibole, packed in the bottom of a Gooch crucible to the depth of not over 1/8 in. After passing the contents of both flasks through the filter, the two residues are shaken with more fresh carbon disulphide and set aside for 24 hours without disturbing, or until it is seen that a good subsidence has taken place, when the solvent is again decanted upon the filter. This washing is continued until the filtrate or washings are practically colourless.

The crucible and both flasks are then dried at 125° and weighed. The filtrate containing the bitumen is evaporated, the bituminous residue burnt, and the weight of the ash thus obtained added to that of the residue in the 2 flasks and the crucible. The sum of these weights deducted from the weight of the substance taken gives the weight of bitumen extracted.

In the analysis of hard asphalts or tar pitch for their solubility in carbon disulphide, and also in the analysis of any of the bitumens for their solubility in naphtha, it is recommended that from 15 to 20 grm. of glass beads be introduced into the first flask with the substance. When the flask is shaken, these beads grind upon any hard lump of bitumen, and thus greatly facilitate the solution of the soluble constituents. In filtering these solutions through the Gooch crucible, they should be allowed to run through by gravity, as the application of an exhaust appears to cause a clogging of the filtering medium.

This test shall be carried on at a temperature of from 20° to 25°. When carbon disulphide or carbon tetrachloride are used as solvents, they must be chemically pure. When naphtha is employed, the committee recommends that in all cases it be described by stating its sp. gr. and the temperatures between which it distils.

For rapid work the committee suggests the following method as a convenient one to be employed. It is based, in general, upon the standard method, and is applicable to practically all bituminous compounds.

From 1 to 10 grm. of water-free material (depending upon the amount of bitumen present) are weighed into a 150 c.c. Erlenmeyer flask, the tare of which has been previously ascertained, and treated with 100 c.c. of carbon disulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside for not less than 15 hours. At the end of this time the contents of the flask are decanted off upon a weighed Gooch crucible fitted with a long-fibre amphibole asbestos filter. The residue remaining in the flask is then washed with 50 c.c. of carbon disulphide, allowed to settle, and decanted as before, the insoluble matter being finally brought upon the filter and washed with 100 c.c. carbon disulphide or until the washings are practically colourless. The filter and contents are then dried at 125°, cooled and weighed. Should any residue remain in the flask, it is also dried and weighed and this weight added to that of the residue in the crucible. The filtrate should be burned off and ignited to an ash, and the weight of the ash thus obtained added to that of the insoluble residue. The weight of the total residue deducted from that of the original material gives the weight of the bitumen soluble in cold carbon disulphide. In case of tars and pitches the percentages of insoluble residue, determined as above, minus that of any ash which may be found by igniting a separate sample, is reported as free carbon. Glass beads may be employed in the flask, as described in the standard method for the determination of bitumen. This test shall be carried on at a temperature of from 20 to 25°.

Penetration.—The consistency, or penetration, of a bitumen shall be the distance, expressed in hundredths of a centimetre, that a No. 2 needle will penetrate into it at 25° (77° F.), in 5 seconds of time, under a weight of 100 grm., the needle to penetrate direct without friction.

Loss on Heating.—The loss of heating of oil and asphaltic compounds shall be ascertained in the following manner: 50 grm. of the water-free material shall be placed in a circular tin box with vertical sides, measuring about 1 in. in depth by 2⅜ in. in diameter, internal measurement. The penetration of the material to be examined shall, if possible, be determined at 25° in the manner heretofore described, and the exact weight of the sample ascertained. The sample in the tin box shall then be placed in a hot-air oven, heated to 170°, and kept at this temperature for 5 hours. At no time shall the temperature of this oven vary more than 2° from 170°. When the sample is cooled to normal temperature, it shall be weighed, and the percentage of loss by volatilisation reported. The penetration of the residue shall then, if possible, be determined at 25°, in the manner heretofore described, and the loss in penetration determined by subtracting this penetration from the penetration before heating.

Standard Method of Estimation of Residual Coke in Bituminous Compounds

This estimation shall be made according to the method described for coal in the *J. Amer. Chem. Soc.*, 1899, **21**, 1116. The method is as follows: place 1 grm. of pure bitumen, free from water, in a platinum crucible weighing 20 to 30 grm. and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for 7 minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the estimation should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon.

The residue minus the small impurity of ash in the pure bitumen is the fixed carbon, which should be calculated to 100% with the volatile hydrocarbons, excluding the inorganic matter.

Standard Method of Sizing and Separating Aggregate in Asphalt Paving Mixture

The method consists of passing the mineral aggregate through several sieves of the following sizes:

	INCHES IN DIAMETER
10-mesh per linear inch, size of wire	0.027
20-mesh per linear inch, size of wire	0.0165
30-mesh per linear inch, size of wire	0.01375
40-mesh per linear inch, size of wire	0.01025
50-mesh per linear inch, size of wire	0.009
80-mesh per linear inch, size of wire	0.00575
100-mesh per linear inch, size of wire	0.0045
200-mesh per linear inch, size of wire	0.00235

The following methods, unless otherwise specified, are those proposed by Clifford Richardson.

Water, Ordinary Method.—Ordinarily it is sufficiently accurate to weigh out 2 to 5 grm. of the material in a crucible, preferably on a watch-glass, to expose more surface, and to subject it to a temperature of 100° in a well-regulated water-bath, until it ceases to lose in weight to an extent of more than 0.2 to 0.3% on successive heatings. A greater concordance is not sought, as many asphalts continue to lose light oils at this temperature. The degree of fineness to which the crude asphalt should be reduced before weighing out is dependent upon the amount of water it contains. In powdering some asphalts, such as crude Trinidad, the material, since it contains 29% of water in emulsion with bitumen, begins to lose water at once. It can, therefore, only be broken into coarse lumps and not reduced to a powder until after a preliminary determination of the water thus lost by the coarse material. Other asphalts, containing only a small amount of hygroscopic or adventitious water, may be ground up at once, while some which are not readily powdered may be cut into small pieces. (If it is necessary to estimate the water absolutely, it may be estimated by a method of distillation as given by Marcusson, or by the Sadtler method in the *J. Ind. Eng. Chem.*, 1910, **2**, 66.)

Alternate Method.—For asphalts such as crude Trinidad, in which the difficulties described are met, a different method of procedure is advisable. The substance is very quickly reduced to a coarse powder only in a mortar provided with a cover, through which the pestle passes. 5 grm. of it are spread out on a 4-in. watch-glass, and this is placed *in vacuo* over sulphuric acid for 12 hours and the loss determined. It should then be reground to a fine powder and exposed again *in vacuo* until it ceases to lose weight. The loss may be stated as water.

In whichever way the asphalt is dried a sufficient quantity is prepared and preserved in this condition in a tightly stoppered bottle, for analysis. Asphalts which cannot be reduced to powder are used in mass.

Refined Asphalts.—Examination of refined asphalts in their most extended form include the determinations given on the accompanying form, used as a convenience in reporting. With well-known asphalts but a limited number of determinations are necessary for the purpose of detecting lack of uniformity or peculiarities in the material.

Physical Properties

Sp. gr., 25.5°/25.5°; original substance, dry
Sp. gr., 25.5°, pure bitumen
Colour of powder or streak
Lustre
Structure
Fracture
Hardness, original substance
Odour
Softness
Flows
Penetration at 25.5°

Chemical Characteristics

Original substance:
  Loss, 100°, 1 hour
Dry substance:
  Loss, 162.7°
  Character of residue
  Penetration of residue at 25.5°
  Loss, 204.4°, 7 hours (fresh sample)
  Character of residue
  Penetration of residue at 25.5°
  Bitumen soluble in CS_2, air temperature
  Organic matter insoluble
  Inorganic or mineral matter
Malthenes:
  Bitumen soluble in 88° naphtha, air temperature
  (This is given in % of total bitumen)
  % of soluble bitumen removed by H_2SO_4
  % of total bitumens as saturated hydrocarbons
  Bitumen soluble in 62° naphtha
  (This in % of total bitumen)
Carbenes:
  Bitumen insoluble in carbon tetrachloride, air temperature
  Bitumen soluble in carbon tetrachloride, air temperature
Bitumen yields on ignition:
  Fixed carbon
  Sulphur
  Ultimate composition
Remarks:

The comprehensive scheme for the analysis of asphalts and fluxes is taken from "The Asphalt Pavement," by Clifford Richardson, Wiley and Sons, New York, 2nd ed., 1908. This is done for the reason that the methods are quite practical and briefly stated and probably represent recent practice better than any other scheme that has been published.

Physical Properties—Sp. Gr.—The sp. gr. of the dried asphalt is taken in a pycnometer at 25°, and referred to water at the same temperature.

Several modifications of the ordinary pycnometer have been proposed for special use in asphalt sp. gr. determinations. The first is the Sommer hydrometer, in which a small metal cup holding exactly 10 c.c. is filled with the bituminous substance in the melted state and then attached to the special hydrometer used. The sp. gr. is read directly and is accurate to the third decimal place.

A second method to that of the Hubbard pycnometer, in which the bituminous substance is melted in a heavy straight walled glass tube, having a neck ground to receive a glass stopper, provided with a vertical opening through its entire length, and having a mark etched upon it. The bituminous material is melted and carefully poured into the pycnometer filling it about half full. After cooling to 77° F. it is weighed then filled with water to the mark and weighed again. The sp. gr. may then be calculated from the formula $\frac{c - a}{(b - a) - (d - c)}$, when *a* represents the weight of the pycnometer empty, *b* its weight filled with water, *c* its weight containing the bituminous substance and *d* its weight containing the bituminous substance and then filled to the mark with water.

The third method is that of the Weiss sp. gr. pan. This pan is of platinum or nickel and hangs supported by a waxed silk thread. The melted bituminous substance is poured into the pan without filling it to any prescribed height. It is weighed in air and then in water at 77° F. The sp. gr. is calculated from the formula $\frac{(c - a)}{(b + c) - (a + d)}$, when *a* represents the weight of the pan in air, *b* its weight in water, *c* its weight plus the bituminous substance in air, and *d* its weight plus the bituminous substance in water. All three of these forms of apparatus are described and figured in Abraham, Asphalts and Allied Substances, 1918, pp. 489 and 490.

The usual determinations of the outward physical features of any mineral substance, colour of streak, structure, fracture, hardness, and odour, if any, are noted.

The colour of the streak or of the powder of a hard asphalt is in certain cases characteristic. For example, in the case of refined Trinidad lake asphalt the powder is a bluish-black colour, while that of the refined Trinidad land asphalt is much browner. Powdered gilsonite is of a very light-brown colour. Powdered grahamite is quite black.

The structure of a solid native bitumen may be either homogeneous or it may show the presence of cavities containing gas, particles of adventitious mineral matter, shale or clay, or other peculiarities.

The fracture may be, in the case of very pure bitumens, conchoidal or semi-conchoidal, pencillated, or hackley in the case of grahamite, or irregular.

The hardness of the original material, if it contains much mineral matter, may be stated in degrees of Mohr's scale, that of the pure bitumen in several ways. It is either brittle, like glance pitch, or soft enough to be penetrated with the needle of a penetration machine, in which case the hardness is expressed in degrees of this machine.

The odour in the case of many bitumens is characteristic. That from Venezuelan asphalt, found near the Gulf of Maracaibo, is extremely strong and rank, while others are more purely asphaltic, especially on warming. The heat, in any case, brings out the odour to a degree not observed in the cold material.

Loss on Heating.—It is sometimes necessary to determine the loss which an asphalt suffers on heating for a time to a definite temperature. The length of time has been arbitrarily taken as seven hours, and the temperature 162.7° and 204.4°.

The determination is made as follows: In a No. 1 crystallising dish, 2¼ in. in diameter and 1 5⁄16 in. high, are placed 20 grm. of the material under examination.

Should it be necessary to use a very much larger dish the weight of the material to be taken should be calculated, so that the volume which it holds shall bear the same relation to the surface exposed as in the case with the smaller dish. It is necessary to take separate portions of the substance for each determination, and not to attempt to determine the loss at 204.4° from the sample which has been previously heated at 162.7°.

The dish is heated to the requisite temperature for the given length of time in an oven, the temperature of which is uniform in all parts.

Softening and Flowing Points.[1]—The solid native bitumens can have no definite m. p. for the reason that they are composed of mixtures of hydrocarbons. It is only possible, therefore, to determine rather arbitrarily the points at which the material softens and flows, and with special reference to the relation of these points toward some standard bitumen. They are determined as follows:

A crystallising dish, of the same form as that used for determining the loss on heating at 162.7° and 204.4°, is placed upon a ring-stand over an asbestos plate or wire gauze where it can be heated by a small flame. It is then filled with clean metallic mercury to a distance of ¼ in. from the top. On the surface is placed a thin microscope cover-glass, No. 00, carrying the specimen of asphalt under examination, and a second glass containing a sample of known softening point as a standard of comparison. The complete apparatus consists of a crystallising dish as above described, a funnel with its stem cut off close to the angle to serve as a cover, a few microscopic cover-glasses, and a thermometer.

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[1] A form of oven now used for heat determinations with asphalt samples has a shelf suspended by a vertical shaft midway in the oven which is revolved by mechanical means at the rate of from 5 to 6 r.p.m. In this way a greater uniformity in the heating of the samples can be obtained.

The specimens are prepared for the experiment in the following manner: When dealing with hard asphalts that can be ground rather coarsely, minute fragments are spread on the cover-glass and placed upon the surface of mercury, covered with a funnel, and a thermometer passed through the orifice of the funnel until the bulb is immersed in the mercury. It is held in position by a clamp attached to the ringstand holding the dish. A burner that can be regulated to a small flame is placed under the dish, and it is heated so that the rise of temperature will not be more than 2 to 3° F. per minute. In a short time it will be noticed that the specimens will have changed from the brown or the yellowish-black colour of the powder to that more nearly approaching the original, with a slight rounding of the individual grains. This is taken as the softening point. On further heating, these globules flow together and form a thin sheet on the glass. The point at which the specimens begin to soften and the beginning of the flow, as indicated by the thermometer, are noted as the softening and flowing points.

Asphalts that cannot be ground are treated as follows: The material is softened and pulled out to a thread 1 mm. in diameter and several small pieces 1 mm. in length cut from it. These should be placed on the glass together, as one will serve as a check on the other and thereby lessen the chance of error. The softening point may be noted by the rounding of the particles and the beginning of the flow, or when the specimen begins to spread out, which is always at the point of contact with the cover-glass, is set down as the flowing point or the temperature at which the specimens will flow perceptibly.

Other asphalt chemists, and notably the committee on asphalt of the "American Society for Testing Materials," have however adopted melting point methods other than the softening point methods of Richardson, and these are in current use.

The first of these methods is "the ring and ball method." The apparatus consists of a brass ring $\frac{5}{8}$ in. in diameter, $\frac{1}{4}$ in. deep, $\frac{3}{32}$ in. wall suspended 1 in. above the bottom of the beaker; a steel ball $\frac{3}{8}$ in. in diameter weighing between 3.45 and 3.50 grm., a standardised thermometer and a 600 c.c. glass beaker. Carefully melt the sample and fill the ring with the material to be tested, removing any excess.

Place the ball in the centre of the ring and suspend in the beaker containing 400 c.c. of water at a temperature of 5°. Set the thermometer bulb within ½ in. of the sample and at the same level. Apply heat uniformly, preferably with an electric hot plate over the bottom of the beaker sufficiently to raise the temperature of the water 5° per minute. Record the temperature at starting the test and every minute thereafter until the test is completed. The softening point is the temperature at which the specimen touches the bottom of the beaker. For temperatures above 99° glycerin should be used instead of water. Tests should check within 3°.

Another method, more generally used for tar pitches but sometimes used for asphalts, is the so-called "cube method." A cube of the material prepared in a brass cubical mould is fastened upon the lower arm of No. 12 gauge wire bent at right angles and suspended besides a thermometer in a tall covered beaker. This is set in a larger beaker containing a liquid and arranged to be heated from below. Heat is applied so that an increase of 5° takes place per minute. The temperature at which the bitumen touches a piece of paper placed in the bottom of the inner beaker is taken as the melting point.

Still another method is the so-called "General Electric method," in which the bituminous material is moulded so that it covers completely and uniformly the short bulb of a thermometer graduated to 500° F. This thermometer is fitted by a cork into a large test tube with side tubular and the test tube immersed in commercial sulphuric acid contained in a large beaker. The m. p. is noted on the thermometer when the bituminous material flows sufficiently that a tear strikes the bottom of the tube.

Estimation of Total Bitumen.—1 grm. of the dried or refined material in a state of very fine powder, if possible, is weighed out and introduced into a 200 c.c. Erlenmeyer flask of Pyrex or Jena glass and covered with about 100 c.c. of carbon disulphide. It is then set aside for at least five hours or overnight, at the temperature of the laboratory. In the meantime a Gooch crucible is prepared with an asbestos felt and weighed. This Gooch crucible is of special form with a large filtering surface. It holds 30 c.c., and is 4.4 cm. at the top, tapering to 3.6 cm. at the bottom and 2.6 cm. deep. This is much better for percolation work than the usual narrow form of Gooch. It is furnished by Eimer and Amend, New York. The felt is made by beating up long-fibre Italian asbestos in a mortar, and suspending the finer particles in water and quickly pouring off from the coarse particles. Too much of the latter should not be removed, or the felt will be too dense. The decanted asbestos and water can be kept in a bottle for use. To prepare the felt, the asbestos and water are shaken up and what is found to be a proper amount poured into the crucible, which has in the meantime been attached to a vacuum filtering flask by the proper glass and rubber connections. As soon as the asbestos has somewhat settled the vacuum-pump is started and the felt firmly drawn on the bottom of the crucible. It is then dried, ignited, and weighed.

After standing a proper time, the disulphide is decanted very carefully upon the filter, which is supported in the neck of a wide-mouthed flask, and allowed to run through without pressure. The flask, after being tipped to pour the first portion, is not again placed erect in order to avoid stirring up the insoluble material, but is held at an angle on any suitable base, such as a clay chimney. After all the disulphide is decanted more is added, and the insoluble matter shaken up with it. This is allowed to settle and decanted as before, the insoluble matter being finally brought on the filter and washed with the solvent until clean. The excess of disulphide is allowed to evaporate from the Gooch crucible at the temperature of the room. The crucible is then dried for a short time at 100° and weighed. The loss of weight is the percentage of bitumen soluble in CS_2.

An alundum filter cone of porous grade may also be used to advantage if more convenient or available.

In the meantime, however, the disulphide which has passed the filter is allowed to subside for 24 hours, if possible, and is then decanted carefully from the flask from which it has been received into a weighed platinum or unweighed porcelain dish. If there is any sediment in the flask, it must be rinsed back into the Gooch crucible with disulphide, and the crucible again washed clean. The solvent in the dish is placed in a good draught and lighted. When all the disulphide has burned, the bitumen remaining in the dish is burned off over a lamp, and the mineral residue, which was too fine to subside, is weighed, if the burning was done in a platinum dish, or dusted out and added to the crucible if in a porcelain one. In the former case the weight is added to that of the Gooch crucible, or subtracted from the % of the bitumen, found without its consideration. Care must be used in this method of procedure that the solvent does not creep over the sides of the crucible and that the outside is free from bitumen before weighing. In order to avoid this, the crucible is supported in the neck of a flask with three constrictions, the neck extended above the top of the crucible and the latter being covered with a watch-glass. (These flasks are made for Mr. Richardson by E. Machlett & Son, 143 East 23d Street, New York.)

Mineral Matter or Ash.—1 grm. of the same sample of material used for the estimation of bitumen is weighed out in a No. 0 porcelain crucible and burned in a muffle or over a flame until free from carbon. This must be determined by breaking up the cake of ash, moistening with water or alcohol, and observing if any black particles of coke are present. The weight of the residue is stated as inorganic or mineral matter.

The estimation is, of course, not exact, sulphuric acid and the alkalies being volatilised in many cases, but it is satisfactory for technical purposes.

The fixed carbon (or residual coke) determination has already been described (see p. 139).

Organic Matter Insoluble.—The amount of this material, sometimes stated as organic matter not bitumen, is obtained by difference; that is to say, by subtracting the sum of percentages of bitumen and inorganic matter found from 100. It, of course, includes all the errors in these 2 estimations, and as the error in the bitumen is one making the percentage too high, and in that of the mineral matter too low, the errors are cumulative, do not neutralise each other, and the percentage of organic matter not bitumen is thus always too high.

If hot carbon disulphide, chloroform or spirits of turpentine are used as solvents for the bitumen, the amount obtained on extraction is somewhat greater, but in technical work the results are no more desirable and such solvents are not often used, as chloroform is expensive where a large number of estimations are carried out, and the spirits of turpentine are so much more viscous that they filter much less readily, while the residue of this solvent remaining on the filter must be removed by naphtha and not by evaporation.

The sum of the 3 estimations, bitumen soluble in CS_2, organic not soluble, and inorganic matter, is, therefore, always 100%.

Naphtha-soluble Bitumen.—For the purpose of determining the percentage of bitumen soluble in naphtha, distillates of 88° and 62°

Bé. are used. It is extremely important that these naphthas should be of the exact degrees specified, since differences in density will make appreciable differences in the amount of bitumen extracted. The distillate should be that obtained from a petroleum with so-called paraffin base. The density of each lot should be carefully determined with a Westphal balance at 15.5°, and if it is too dense it should be rejected. On the other hand, if it is too light it can be brought to the proper density by blowing a current of air through it for a short time, at the ordinary temperature in the case of the 88° and, after slightly warming it, in the case of 62° naphtha. Redistillation of these naphthas is unnecessary, as the products of the distillations are no more uniform than the original naphthas.

It will be found very necessary that hard bitumens should be reduced to an impalpable powder before attempting to extract them, as otherwise the extractions will not be complete. The softer bitumens should be divided as much as possible.

The bitumen is usually extracted with naphtha of both densities in order to determine the differences in their action. If the amounts extracted by each is the same or nearly the same, it will point to the fact that the bitumen consists of hard asphaltenes mixed with light malthenes, the latter equally soluble in naphtha of both degrees of sp. gr., and but little of intermediate hydrocarbons, or of the very hard asphalt fluxed artificially with some light oil. If, on the other hand, there is a very considerable increase in the percentage dissolved by the 62° over the 88° naphtha it may be assumed that the malthenes are well-graded and natural constituents of the bitumen which is being examined. In certain cases, however, the use of the two naphthas is unnecessary. It would be useless to extract a maltha with a dense naphtha or glance pitch or albertite with a lighter one.

It appears, therefore, that heating increases the density of naphthas, and consequently their solvent powers (from inability to condense the more volatile parts) but that the change in the 62° naphtha is small, so that it can safely be heated to a slight extent.

As a result of these experiments all determinations are now made with cold naphtha by the following method:

1 grm. of the substance is weighed into a 200 c.c. Erlenmeyer flask, covered with naphtha and allowed to stand, as in estimating total bitumen; in fact, the entire process is the same, with the exception

that one or two precautions must be observed. It is well not to attempt to break up any lumps with a stirring rod, as the substance, especially the softer asphalts, may then adhere to the rod or flask and be difficult to detach.

It may also be necessary to treat the substance with several portions of the solvent instead of with 2 or 3, as in the case of carbon disulphide. No heat is applied at any time on the process.

Fixed Carbon.—The fixed carbon is determined usually on the pure bitumen according to the method recommended by the Committee on Coal Analysis of the Amer. Chem. Soc. (See p. 139.)

FIXED CARBON IN BITUMENS

	Extremes		High grade
	High	Low	
Grahamite	53.3	35.3	53.3
Albertite	54.2	29.8	29.8
Gilsonite	26.2	3.3	14.5
Manjak Barbadoes			15.0
Asphaltenes from Trinidad bitumen			25.8
Glance pitch	30.0	15.0	15.0[1]
Asphalt	17.9	10.8	14.2
Byerlyte (artificial asphalt)			14.3
Standard Asphalt Co's. mine, soft gilsonite			17.3
Malthenes from Trinidad bitumen			6.3
Wurtzilite, Utah	6.8	5.3	8.2
Residuum, Pennsylvania field			3.4
Sunset oil, Kern Co., Cal			2.7

[1] Egyptian.

The residue, minus the small impurity of ash in the pure bitumen, is the fixed carbon, which should be calculated to 100% with the volatile hydrocarbons, excluding the inorganic matter. As the committee states, this determination, like most industrial ones, is arbitrary, but it is of the greatest value in determining the nature of a bitumen quickly. Experience has shown that true hard asphalts have never been found which yield more than 17.9% nor less than 10.0% of fixed carbon, whilst grahamite yields over 53%, albertite over 29 to 54%, and some other bituminous materials characteristic amounts of fixed carbon.

Estimation of the Amount of Hard Paraffin Scale.—The amount of hard paraffin scale contained in any flux or heavy oil can be readily estimated by Richardson's modification[1] of the method of Holde.[2]

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[1] *J. Soc. Chem. Ind.*, 1902, 21, 690.

[2] Mitt. a. d. könig. tech. Vers.-anst., Berlin, 1896, 14, 211. Abs. *J. Soc. Chem. Ind.* 1897, 16, 362; Lunge, Chem. Tech.; Untersuchungs Methoden 3, 9.

The method in detail is as follows:

The Estimation of Paraffin in Petroleum Residues, Asphaltic Oils, and Asphalts Fluxed with Paraffin Oils.—For this purpose, 1, 2, or more grm. of the substance to be examined is taken and covered with 100 c.c. of 88° naphtha in an Erlenmeyer flask. The amount will depend on the amount of paraffin present and on the percentage of oil which remains after the preliminary treatment with naphtha and acid. Several grm. can be taken of a Trinidad asphalt cement, made of asphaltum and Pennsylvania residuum, which contains 26.0% of mineral matter and only 70.0% of its bitumen is in a form soluble in 88° naphtha.

The object of the naphtha treatment is to separate the paraffin from substances of a non-bituminous nature and from some of the asphaltic hydrocarbons insoluble in naphtha which would be precipitated in the ether alcohol solvent and contaminate the paraffin.

The naphtha is allowed to act on the substance overnight, and the next morning the solution is decanted through a Gooch crucible. The residue is washed well with naphtha, and the combined solution and washings united. If desired, the residue, insoluble in naphtha, remaining on the asbestos felt, can be weighed and the amount of soluble bitumen determined by difference. In the case of carefully prepared residues from paraffin petroleum, this naphtha solution may be evaporated in the flask in which the paraffin is to be separated, and the subsequent determination by the Holde method carried on with this residuum or bitumen soluble in naphtha, but the results obtained are too high. Where asphaltic oils are present in the naphtha solution bitumen, and preferably in all cases except those of distillates, a further treatment is necessary to remove oils, which would otherwise be thrown out, from the ether solution with the paraffin by the alcohol. For this purpose the naphtha solution is placed in a separating funnel and shaken with sulphuric acid, sp. gr. 1.84, until a fresh portion of acid is but slightly coloured. Twice is generally sufficient. The solution is washed with water several times, then with a weak solution of sodium carbonate, again with water, and the bitumen in solution recovered, weighed, if desired, and treated by the Holde[1] method for the separation of the paraffin it contains. By this means all the unsaturated hydrocarbons and those of an asphaltic nature, readily precipitated by alcohol from their ether solution, are removed, and the possibilities brought about of recovering the paraffin in a pure condition.

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[1] See description of Holde method under "Analysis of Crude Petroleum."

The paraffin recovered after treatment was white and pure, whilst that obtained in the other way, even by distillation *in vacuo*, was coloured. The results after treatment were, of course, lower and more correct.

In this way it can be determined whether the flux which has been used in the preparation of an asphalt cement has been derived from a paraffin petroleum or from one having an asphaltic base, since, if paraffin is found to such an extent as shown, it will necessarily point to the use of a paraffin flux, as no native solid bitumen in use in the paving industry contains paraffin.

Non-bituminous Organic Matter and Ash.—As noted above, the organic matter not soluble in the various solvents used for fractionating the asphalt is noted as "non-bituminous organic matter" or by some similar descriptive term. It is estimated by difference; the total residue left after the various solvents have exhausted their action is dried, ignited until all carbon has disappeared, and weighed again. The loss of weight has been by most authorities considered to be non-bituminous matter. It has been found by Richardson, however (*Proc. Am. Soc. Test. Mat.*, 1906, **6**, 509), that clays absorb certain amounts of bituminous matter, so that what has generally been considered organic non-bituminous matter[1] is probably bituminous and should be largely included with the amount of bitumen found. It is obvious that if the original matter contained notable amounts of carbonates, the total loss will include the carbon dioxide that has escaped. To correct this, the ash may be recarbonated by allowing it to remain some hours in contact with a solution of carbon dioxide in water, or by heating it with ammonium carbonate solution, evaporating, and heating gently. Ash may, of course, be determined directly, without extraction. This will give a more accurate result in some cases, in consequence of the solubility of some of the mineral material in the solvents used. The detailed examination of the ash is conducted according to the usual methods for clay, limetones, or sand stone, as the case may be.

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[1] F. C. Garrett in a private communication to the former reviser of this section seems to differ in opinion from Clifford Richardson who considered the organic non-bitumen that had previously been reported as non-existent and due to the adsorptive effect of the mineral matter. Garrett examined it microscopically and found it to consist largely of vegetable matter (cellulose, etc.).

Sulphur.—Richardson recommends Mabery's method—combustion in a current of oxygen and absorption of the sulphur dioxide by standard alkali. Day (*J. Frank. Inst.*, 1895, **140,** *221*) found considerable difficulty in determining sulphur in a specimen of Utah gilsonite, owing to the liability of sulphur compounds to distil before oxidation. He finally succeeded by oxidising the material in an open vessel with strong nitric acid by aid of heat. In time the material dissolves completely to a dark red liquid. When this condition is reached, the solution should be poured into cold water, by which a reddish-brown precipitate is formed, which contains all but traces of the sulphur. This mass is well-washed, and the sulphur determined by Eschka's method.

E. H. Hodgson (*J. Amer. Chem. Soc.*, 1898, **20,** 882) has made tests of several methods for estimating sulphur in asphalts, and finds that Carius' method—oxidation by fuming nitric acid—gives the best results, but is tedious and liable to explosion. This process is thus described: The tubes used were made of heavy glass. Three determinations are started on each sample, one with from 1 to 2 grm. of oil, depending upon the amount of sulphur expected, the others with less. The sample, in a small bulb blown from small-bore tubing, is placed at the bottom of the Carius' tube. To fill, the bulb is heated to expand the air in it and allowed to cool with the end which is drawn down to a capillary held under the oil, both while heating and as it cools. After the sample bulb is at the bottom of the tube, 15 c.c. of fuming nitric acid (sp. gr. 1.60) are poured on. The open end is then drawn out fine, but not sealed, endeavouring while doing so to thicken the walls by allowing them to be drawn together, rather than become thin by being pulled out too quickly. The tube is then heated for about 6 hours in water kept at from 80° to 90°, 5 c.c. more of acid are added, the tube is sealed, and heated in a guarded oven (on account of danger of explosion) at 150° for from 4 to 5 hours. Allow the tube to cool, open, reseal, and heat again for from 2 to 4 hours at a temperature of 180° to 200°. Cool, open, and remove the liquid to a beaker of 250 c.c. capacity; dilute with water, filter, and wash. If the residue contains anything but sand, it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of sodium hydroxide. The nitrates are completely decomposed by repeatedly evaporating the solution with hydrochloric acid and the silica rendered insoluble by heating to 110° in an air-bath. The mass is cooled, 2 or 3 c.c. of hydrochloric acid added, then 100 c.c. of water, the mixture stirred, filtered, the filter well washed, and the filtrate diluted to 200 c.c., heated to boiling, and 20 c.c. of a 20% solution of barium chloride added from a burette at the rate of about 1 drop each second, stirring all the time. After the barium chloride has been added, boil for about 10 minutes and then allow to stand 24 hours. Filter, wash with hot water, dry, ignite, cool, moisten with sulphuric acid, re-ignite, cool, and weigh.

The double crucible method of S. S. Sadtler described on page 87 is perfectly applicable for asphaltic materials of all kinds, and in fact it is more suited for this class of materials than for crude oils, for with very volatile compounds precautions are necessary to prevent too rapid volatilisation of the oil.

The methods employing sodium dioxide or nitrates are apt to give results too low.

ULTIMATE COMPOSITION OF ASPHALTS

The ultimate composition of an asphalt will, as a rule, be of little value in determining its application in engineering or industrial operations. The amount of sulphur and nitrogen may be of some moment. The former is regarded by Richardson as influencing materially the hardness of the asphalt by inducing polymerisation, but this view has not been accepted by all experts in this field. The oxidation of the sulphur, which is probably mostly present in combination with hydrocarbons, in forms analogous to the mercaptans, may produce acids which will injure the asphalt proper or the paving mixtures made with it. Nitrogen is usually present in small amount, and, in part at least, in the form of pyridine derivatives.

The following explanation of the absence of oxygen is quoted from Richardson (*J. Soc. Chem. Ind.*, 1898, **17**, 29).

"According to Dana's Mineralogy, 'asphaltum or mineral pitch is a mixture of different hydrocarbons, part of which are oxygenated;' and it is stated that 'the fluid kinds change into the solid by the loss of a vaporisable portion on exposure, and also by a process of oxidation, which consists first in a loss of hydrogen, and finally in the oxidation of a portion of the mass.' Many other writers on the subject also express the same views. For the purpose of determining how far these statements were to be relied upon, since my earlier investigations of the bitumens of Trinidad, Bermudez, and some other asphalts had not shown that they contain oxygen, I have had complete ultimate analyses made of most of the pure bitumens previously examined for sulphur, and the results have been given in the same table. It is evident that among this large number of malthas and asphalts there are none, the soluble bitumen of which contains oxygen to an appreciable extent, although they all contain sulphur and nitrogen. It is, however, easy to explain how the earlier analyst reported oxygen as a constituent of many asphalts. As shown by several recent investigators, the complete combustion and estimation of carbon and hydrogen in the higher hydrocarbons is an extremely difficult thing, the tendency being toward the formation of acetylene and unsaturated hydrocarbons instead of carbonic acid and water, so that there is a deficiency in the amount of the latter found in an analysis, unless the greatest care is used. This had been commonly and naturally stated as oxygen. At the same time most analyses ignored the presence of sulphur and nitrogen, so that the amount of these elements is included in the stated percentage of oxygen. It is not surprising, therefore, that oxygenated hydrocarbons are frequently spoken of as occurring in asphalt, and it is equally plain that none exist in the bitumens of which they are composed. With the amount of sulphur present in most of them this is not surprising, as this element easily substitutes oxygen in most of the hydrocarbon derivatives."

The following figures are taken from results given by Richardson (*J. Soc. Chem. Ind.*, 1898, **17**, 29) who gives all the elements present in the bituminous matter. In each case the percentage is calculated upon the extracted bitumen.

The figures for the sulphur are instructive when compared with the consistence. As a rule, it is highest in hard asphalts and lowest in malthas.

ULTIMATE COMPOSITION OF THE BITUMEN OF ASPHALT, MALTHAS, ETC. (HARD ASPHALT)

	Consistence	In extracted bitumen				
		S	C	H	N	Total
Nevada	Pitch	9.76	79.58	9.31	1.30	99.95
Texas, Uvalde Company	Hard	9.60	80.32	10.09	0.28	100.20
Italy, Ancona	Pitch	9.39	79.56	8.80	1.40	99.15
Egypt	Pitch	8.52	80.87	10.42	0.19	100.00
Cuba, Bejucal	Pitch	8.28	82.98	9.44	0.09	100.79
California, Waldorf	Hard	6.48	82.77	10.62	0.35	100.21
California, LaPatera	Hard	6.23	83.30	9.88	0.70	100.11
Trinidad lake	Hard	6.16	82.33	10.69	0.81	99.99
Tobago	Pitch	6.16	83.37	10.54	0.50	100.57
Turkey	Hard	6.14	83.98	9.19	0.09	99.40
Montana, hardened	Hard	5.31				
California, Santa Maria	Cheesey	5.69	82.79	11.58	0.48	100.54
Trinidad, land	Hard	4.98	83.65	10.76	0.45	99.94
France, South	Hard	4.78	82.07	11.58	1.56	99.99
Venezuela, Bermudez, hard	Medium	3.93				
Sicily, rock	Medium	3.69	84.95	11.34	0.33	100.31
Kentucky	Medium	3.39	84.16	11.52	1.58	99.65
Texas Rio Grande	Medium	3.28				
Bermudez, hard		3.93			0.75	
Bermudez (maltha)		5.87				
Montana (maltha)		3.92				
Mexico		1.48				
California, Alcatraz (maltha)		1.32			1.21	
Gilsonite, Utah		1.79			0.79	
Albertite, New Brunswick		1.20			0.42	

Bromine and Iodine Absorption.—Endemann obtained the following figures for iodine absorption. No hydriodic acid was formed, hence the iodine all formed additive compounds:

	Trinidad		Mexican
	Land	Lake	
Iodine, %, in 20 hours	20.32	19.04	21.90

Richardson gives numerous observations of bromine absorptions. The following percentages are taken from his tables:

BROMINE ABSORPTION AND SULPHUR IN ASPHALTS, ETC.

	Sulphur	Bromine absorption	HBr
Trinidad oil spring	....	29.21 21.09	18.20 10.87
Trinidad pure bitumen	....	30.42 29.99	12.19 12.58
"Petrolene" Trinidad	3.25	24.46	9.54
"Petrolene" Bermudez	3.01	19.75	8.40
"Asphaltene" Trinidad	10.07	32.89	7.43
"Asphaltene" Bermudez	4 78	25.38	7.35
Bermudez, soft asphalt, middle of lake	5.23	29.71 24.22	19.25 15.31
Burmudez, softer asphalt, middle of lake	5.87	21.80 32.69	13.74 18.89
Bermudez, softest asphalt, middle of lake	....	20.83 26.78	12.49 15.74
Bermudez, oil volatilised from the asphalt	3.31	23.21 23.11	12.21 14.07
Asphaltic maltha, Cal	1.40	23.22 23.73	.... 15.31
Pedernarles refined	2.29	39.16 38.54	16.09 16.83
Alcatraz liquid asphalt	1.32	25.40 29.31	16.95 19.85
Asphalt cement from Berlin surfaçe	....	28.86 25.89	....
Pittsburg flux	4.22	....	....
Kerosene	....	3.18 3.62	....
Petroleum residuum, Penn	0.60	20.80	16.40
Petroleum residuum, Penn	0.46	22.15	15.82
Petroleum residuum, Ohio	2.26	34.07	19.72
Petroleum residuum, Ohio	2.07	33.41	11.23
Asphalt oil distilled *in vacuo*, 210°–220°	1.15	23.07	9.16
Asphalt oil distilled *in vacuo*, 260°	0.84	23.80	7.41
Asphalt oil distilled *in vacuo*, 270°	0.55	21.42	8.82

Nature of the Hydrocarbons in Asphalt.—Richardson has studied the hydrocarbons in Trinidad and Bermudez asphalts by fractional distillations, under conditions which reduce to a minimum the liability to cracking. The lighter oils seem not to contain paraffins, olefines, acetylenes, or naphthenes, but to belong to a dicyclic series.

Artificial Asphalts.—Many attempts have been made to employ the pitches and residua from coal-oil and coal-tar as substitutes for asphalt. Some of these paving mixtures have been laid extensively in American cities, but have generally been unsatisfactory. A few special forms of substitute asphalts deserve notice.

"Pittsburg flux" is produced by heating coal-oil residuum with sulphur; much of the latter is converted into hydrogen sulphide and escapes, but a notable amount is retained. A tough and sticky mass is produced, which melts only at a high temperature. It differs, however, from true asphalt in several important particulars.

"Sludge asphalt" is made from the sludge-tar of the petroleum refinery by the use of sulphur, and resembles asphalt more closely than does "Pittsburg flux."

"Byerlyte" and "Sarco" artificial asphalts are both made from the heavy petroleum oil left after the burning oil has distilled. This is heated gently for five or six days, a current of air being passed through continuously. It contains, of course, no sulphur, but the quantity of oxygen is not large, as much is eliminated in the form of water, produced simultaneously with the polymerisation or thickening of the hydrocarbon part of the residua.

A typical method of this kind is described as follows:

About 3.5 tons of petroleum residue of 18° Bé., are placed in a hooded pan and heated to 193°, whereupon air is blown into the contents through a perforated coil for 40 hours, the volume of air admitted per hour being 5,000–6,500 cu. ft. during the first 32 hours and 3,000–4,000 cu. ft. during the remainder of the time. The mass becomes thicker and an increase in the internal heating is noticeable. The loss in weight amounts to 3.5–4%.

The changes occurring during the operation are shown in the following table, giving the composition of the mass at the different times specified.

The increased proportion of asphaltene marks the improvement of the product for the purpose in view.

	Hours			
	0	16	32	40
	%	%	%	%
Petrolene	...	90 51	74.40	73.34
Asphaltene	...	8.03	23.46	25.14
Other organic matter	2.50	0.85	1.40	0.89
Mineral matter	...	0.61	0.70	0.63

In addition to these substitutes there is the residuum from the distillation of oils with heavy asphaltic bases. In America the products have commercial importance from both California and Texas petroleums. Being sulphur petroleums, the action of sulphur in the hydrocarbons, especially in the case of the Texas oil, produces asphaltic material in addition to that naturally occurring in the oil.

ASPHALT FLUXES

Because of differences (largely of a physical nature) between asphalt fluxes and hard asphalts, a special series of tests is given, as suggested by Clifford Richardson.

PHYSICAL PROPERTIES

- Sp. gr., dried at 100°, 25.5°
- Flows, cold test
- Colour
- Odour
- Under microscope
- Flashes, °, N. Y. State oil tester
- Viscosity, P. R. R. Pipette

CHEMICAL CHARACTERISTICS

- Original substance:
  - Loss, 100°, 1 hour or until dry
- Dry substance:
  - Loss, 162.7°, 7 hours
  - Character of residue
  - Penetration of residue at 25.5°
  - Loss, 204.4°, 7 hours (fresh sample)
  - Character of residue
  - Penetration of residue at 25.5°
- Bitumen soluble in CS_2, air temperature
- Organic matter insoluble
- Inorganic or mineral matter
- Bitumen soluble in 88° naptha, air temperature, pitch
- % of soluble bitumen removed by H_2SO_4
- % of bitumen as saturated hydrocarbons
- % of solid paraffins
- Bitumen yields on ignition:
  - Fixed carbon

The methods used in making these determinations are, as a whole, the same as those described for hard asphalts with the following modifications.

Sp. Gr.—The sp. gr. on oils or fluxes is taken on the material either dried at 100°, or, if there are light oils present volatile at this temperature, on some of the oil freed from water by being swung in the centrifugal.

Heavy fluxes too dense with which to employ a pycnometer are introduced into an open specimen tube, 10 cm. long, 2 cm. in diameter, and holding about 27 grm. of water, even with the top, which is ground flat and parallel to the base. The weight of this volume of oil at 25.5° is compared with that of water at the same temperature. A preferable way of obtaining the sp. gr. of very viscous tars, malthas, etc., is given under "Bituminous Road Material," page 200.

Flow Test.—Some of the oil is chilled in a large test-tube and gradually allowed to attain the temperature of the room. The point at which it will flow in the inclined tube is the flow-point.

Colour.—This is found by examining the reflection from the surface of the cold oil. It is intended to be that revealed by reflection and not by transmission light through a thin film.

Odour.—The odour can be described as that corresponding to different kinds of known petroleum in the cold or on heating.

Microscopic Examination.—The appearance of an oil that has been heated is noted under the microscope to determine the presence of material insoluble in the main mass of the oil.

Flash-point. - The flash-point is determined in a New York State oil tester.[1] The water-bath is of course removed and the oil heated directly with a flame of a size to raise the temperature at the rate of 20° F. per minute, and a small flame from a capillary glass or metal tube is used for flashing. The flame should be applied at 5° intervals. The determination should be repeated on such oils as flash at unexpected temperatures. The water must be removed from the oil or flux before putting it in the tester cup, either by heat or by the centrifugal.

Open tests of high flashing oils are not reliable and, at best, with the closed tester a reading of 5° intervals only need be sought.

Viscosity and Float Test.—The viscosity of bituminous road material asphalt mixtures, fluxed asphalts and road oils is determined in the Engler viscosimeter at any temperature desired. The full quantity, 250 c.c. is placed in the apparatus and raised to the temperature at which it is desired to make the test. 100 c.c. is then permitted to flow into a graduated flask of the above capacity, and the time of the flow in seconds is noted. The result may be expressed either in seconds or by ratio compared with the time of flow of a similar quantity of water at 25°.

Road binders should be too viscous for testing in the Engler apparatus at temperatures below 121.1° to 176.6°, and to determine the consistence of such materials at normal or slightly elevated temperatures the New York Testing Laboratory float apparatus is employed. (*Eng. Rec.*, 1909, **59**, 584.)

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[1] *Eng Rec.*, 1909, 59, 584.

The apparatus, which is made by Howard and Morse, Brooklyn, N. Y., consists of two parts—an aluminium float or saucer, and a conical brass collar. The two parts are made separately for reasons of economy, so that 1 or 3 of the floats will be sufficient for an indefinite number of brass collars.

In using the apparatus, the brass collar is placed upon a brass plate, the surface of which has been amalgamated, and filled with the bitumen under examination, after it has been softened sufficiently by gentle heating to flow freely.

The collar must be completely filled, and as soon as the bitumen has cooled sufficiently to handle, the collar is placed in ice-water at 5° for 15 minutes. It is then attached to a float and immediately placed upon the surface of the water, which is maintained at 32.2° or any other temperature desired.

"As the plug of bitumen in the brass collar becomes warm and liquid, it is gradually forced out of the collar, and as soon as the water gains entrance to the saucer the entire apparatus sinks below the surface of the same.

"The time, in seconds, elapsing between placing the apparatus on the water and when it sinks, is determined most conveniently with a stop-watch, and is considered as the consistence of the bitumen under examination."

Loss at 162.7° and 204.4° in Seven Hours.—Separate portions of 20 grm. of the dried material are taken for each determination and are heated to these temperatures in the manner described for solid bitumens. The residues from these oils which have been so heated are examined as under Asphalts. This is to show whether heat at such temperatures has seriously affected the bitumens.

After cooling, and weighing, the appearance of the residue is noted, especially as to whether it is smooth or granular, (owing to the presence of paraffin), the temperature at which it flows, whether it pulls out to a long string or is short. If it is so hard that it does not flow except on raising the temperature above 37.7°, its consistence is determined with the penetration machine either at 37.7°, or at 25.5°, or at low temperatures.

The residue should be examined under the microscope to determine whether, owing to the nature of the fluxes, they have been at all decomposed at these temperatures with a separation of insoluble pitch, which is an evidence that the original flux must have been more or less cracked in the process of manufacture.

Total Bitumen; Inorganic Matter and Organic Not Soluble; Naphtha Soluble Bitumen.—These determinations are arrived at by the methods already described for hard asphalts.

As the oils and fluxes are more easily soluble, it is unnecessary to let the solvents act on them for so long a time as in the case of hard asphalts. There is little object in using 62° naphtha with oils or fluxes, as there is too little difference between its solvent power and that of carbon disulphide to make it worth while with such materials. The residue insoluble in 88° naphtha, however, shows how much decomposition there has been in fluxes which have been subjected to excessive heat.

Determination of the Character of the Hydrocarbons in Fluxes.—The character of the hydrocarbons in any of the heavy oils used for fluxing purposes is determined by treatment with sulphuric acid by the method described for use with malthenes from hard asphalts.

Physical Tests on Asphalt Mastics and Paving Compositions.—The chief tests applied on samples of the finished preparations are the tensile strength of briquettes with a machine such as is used for testing cement briquettes, and the penetration test with some form of penetrometer. such as that of Bowen.

Tests of Asphalt Lutes and Cement (suggested by Dr. Kohler, "Chemie und Technologie der natürlichen und künstlichen Asphalte): 1. Adhesive power; 2. Water-proof character; 3. Resistance to acids and alkalies; 4. Proof against plant roots; 5. Elasticity; 6. The holding of the most constant plasticity through certain limits of temperature; 7. Resistance to pressure. Figure 15 shows the apparatus used to test the adhesive power. Mercury is allowed to flow from A into B until the weight is sufficient to pull the plates apart.

The water-proof character is shown by carrying water under pressure through terra-cotta pipes, joined together with the asphalt cement.

Roofing Papers.—For the examination of the quantity and the character of the bitumens impregnating materials, the paper is extracted with benzene or carbon disulphide. In estimating the amount of tar used, about 20% is added to the amount extracted for the free carbon that remains in the paper.

The physical tests applied are the thickness, the tensile strength, and degree of resistance to water. The latter test is made by immersing in water for 24 hours and then noting the increase in weight.

As they become older some papers become more porous and the sand, gravel, powdered coke, etc., aids in carrying water through the body of the paper.

Action of H_2SO_4 on Bitumens.—As part of a very extensive scheme of investigation of asphalt pitches, Richardson experimented with the action of sulphuric acid of different strengths on the naphtha-soluble portion of asphaltic bitumens. 2 grm. of each sample were extracted with boiling 88° gasoline and this solution was shaken with 2 amounts of acid in each case, and after the acid treatment washed with sodium hydroxide solution and the results noted.

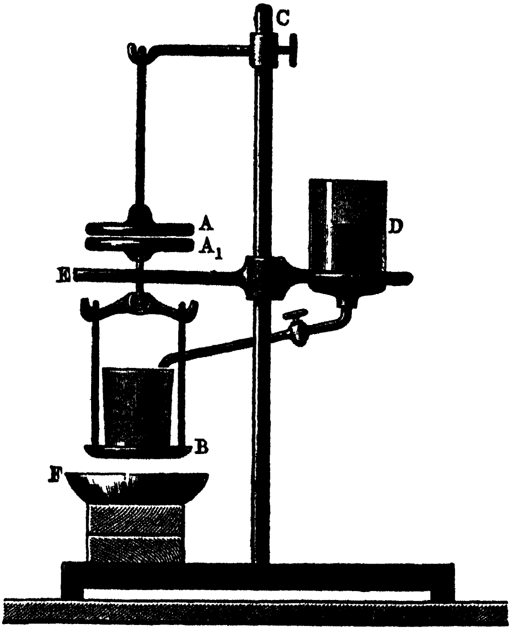

FIG. 15.

PER CENT. OF NAPHTHA-SOLUBLE BITUMEN UNACTED UPON BY ACIDS

	Total bitumen	Naphtha-soluble bitumen	Percentage of total bitumens thus soluble	Percentage of naphtha-soluble bitumens unacted on by acids					
				25 % NaOH	3 to 1 H_2SO_4	2 to 1 H_2SO_4	1 to 1 H_2SO_4	Conc. H_2SO_4	Fuming H_2SO_4 + SO_3
California consolidated	66.9	47.78	71.40	84.8	71.8	67.1	64.4	54.4	4.0
Bermudez lake	96.5	67.27	69.70	80.8	80.7	80.9	78.8	38.9	19.1
Trinidad lake	57.1	34.55	60.50	90.1	89.8	87.0	79.3	38.9	19.1
Alcatraz maltha (1894)	97.9	85.19	87.00	100.0	93.7	88.4	87.0	64.2	35.7
Penn. residuum	100.0	95.68	95.71	97.4	95.5	95.6	95.5	89.5	53.3
Ohio residuum	100.0	97.05	97.10	99.5	94.9	93.4	93.6	86.4	62.6
Russian residuum	100.0	100.00	100.00	100.0	93.6	92.7	92.2	79.3	68.8

or, calculated on another basis,

PER CENT. OF TOTAL BITUMEN REMOVED BY REAGENTS[1]

California consolidated					48.7	52.1	54.0	61.2	97.1
Bermudez lake					43.5	43.6	45.1	72.8	86.7
Trinidad lake					45.7	47.3	52.1	76.5	78.6
Alcatraz maltha					17.7	23.1	24.3	44.2	69.6
Penn. residuum					8.5	8.5	8.5	14.4	49.0
Ohio residuum					7.9	9.4	9.4	16.2	39.2
Russian residuum					6.4	7.3	7.3	20.7	31.2

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[1] More thorough extraction would have increased these percentages in some cases.

Asphalt

Method of Analysis of Total Bitumen in Surface Mixtures.—Weigh 10 grm. in a long tube or deep glass cup with ground stopper and then fill ¾ full with carbon disulphide. Whirl in a centrifuge for several minutes. Decant the solvent into a tared platinum dish and fill the tube ¾ full with fresh carbon disulphide. Stir sediment with a rod and whirl again. This is repeated until the solvent above the sediment remains colourless. Ignite these extracts in a good draught and burn to an ash. Dry the test-tube with the sediment and weigh. Add correction in the platinum dish and subtract from 100% to obtain the bitumen.

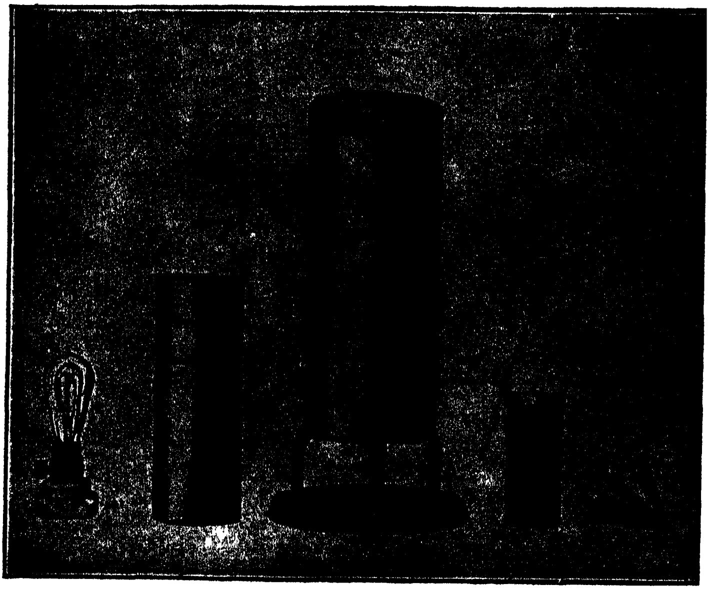

FIG. 16.—N. Y. testing laboratory extractor in parts.

Method of Extracting Bitumens from Binding Courses, Topekas, Etc.—A special extractor (New York Testing Laboratory Type, see Figs. 16 and 17), for analysis of paving mixtures containing broken stone, is used. The bituminous mixture should be warmed until it can be readily broken apart by hand, without fracturing any of the stony particles; 500 grm. of the disintegrated mixture should be packed as tightly as possible in the wire basket and then covered with a disc of cotton or felt of ¼ to ½ in. thick; 175 to 200 c.c. of carbon disulphide, carbon tetrachloride, chloroform or benzol are placed in the inside vessel in which the wire basket is suspended. Cool water should be circulated through the inverted cone condenser which is also the cover of the apparatus and not intended to fit tight. A 16 c. p. carbon filament incandescent lamp is the source of heat. A 500 grm. sample of the mixture should be extracted clean with carbon disulphide in about 3 hours. From 200 to 300 grm. of asphalt block or Topeka type mixture is a sufficiently large sample for that type of material. After extraction, the solvent and matter removed from the sample during the analysis should be burnt to recover any fine mineral particles which may have passed into the extract. The extractors are made entirely of metal.

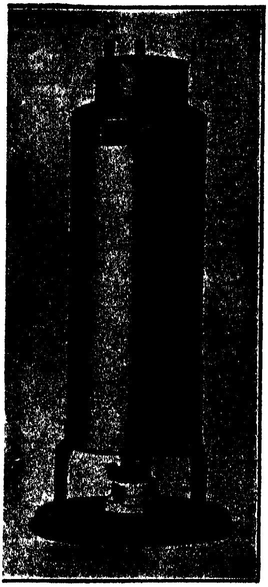

FIG. 17.—N. Y. testing laboratory extractor complete.

Ductility (New York Testing Laboratory Methods).—The sample is melted and poured into brass briquette moulds,[1] the latter first having been amalgamated to prevent the asphalt from adhering. The sample is then cooled and placed in ice water (41° F.) for 15 minutes. Then with a heated knife, the excess of asphalt over 1 cm. thickness is cut off so that the centre and narrowest portion of the briquette is 1 sq. cm. The briquette is placed in water at 77° for 15 minutes, and then drawn out in water at 77° F. in a ductility machine, so regulated that it only moves 5 cm. per minute. The reading on the metre rule, when the thread of asphalt breaks is called the ductility of the asphalt.

Melting-point Apparatus.—Outer vessel or container for the glycerin bath, a 600 c.c. Jena or Pyrex beaker, Griffin type.

Inner vessel or air-bath 200 c.c. is a lipless Pyrex beaker.

Chair or support for inner vessel is cut out of 1/16 in. sheet aluminium.

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[1] Moulds for bitumen and brass collars used in N. Y. T. L. float test apparatus are made by Howard & Morse, Brooklyn, N. Y.

Cover for inner vessel is cut out of sheet aluminium or brass.

Support for moulds consists of discs of brass with holes tapped for two or four moulds suspended on three hangers.

Commercial glycerin, standard thermometer.

Double thickness 20 mesh iron gauze.

Iron tripod, stand and clamps.

Bunsen, or alcohol burner.

Manipulation.—One or more of the brass moulds standing upon a piece of amalgamated brass or tin should be filled with the bitumen under examination. The bitumen may be softened by cautiously heating it in a small casserole or tin box until it is sufficiently fluid to be poured into the mould. After trimming off the upper surface level with the mould, place the sample in water at 77° F. for about 10 minutes. It should then be suspended in the air-bath of the apparatus, and the cover and thermometer placed in their proper positions. The temperature of the glycerin bath should also be 77° F. at the beginning of the test.

The apparatus should stand on a double 20-mesh iron gauze, supported on an iron tripod and heated at the rate of 5° F. per minute. The temperature at which the sample of bitumen flows from the mould and first touches the bottom of the inner vessel, is recorded as the melting or flowing point.

Float Test.—The sample is melted at as low a temperature as possible and then poured into a small brass mould (the same as used in melting point determinations). It is then allowed to cool, placed in water at 41° F. for 10 minutes, the edges then trimmed with a hot knife and cooled for 10 minutes longer. It is then screwed into an aluminium float plate or dish about 3 in. diameter and placed in water at 150° F. starting a stop watch the moment the float is placed in the hot water. The second the water flows through the melted bitumen into the inside of the float mould is taken as the float.

Drip Point.—Melt the sample at as low a temperature as possible and then coat the bulb of a thermometer with the bitumen until a layer 1/8 to 1/16 in. thick and about 1 in. long is obtained. Cool and place in an air-bath free from currents, which is heated so that the temperature of the air rises about 2° per minute. The temperature on the thermometer when the first drop falls, is noted as the drip point.

Roofing Papers[1]

Method of Testing.—(1) Make four tests on Mullen (paper) machine. Report average and temperature. (Cut two 3-in. squares, two 6-in. squares, one piece 6 × 2 in. for subsequent tests.)

(2) Ignite one of the 3-in. squares and calculate per cent. ash.

(3) Extract one 6-in. piece and one 3-in. piece with carbon disulphide in an extractor and calculate per cent. bitumen, etc., as per following formula:

Formula for calculating bitumen, felt and mineral matter in coating.

If A = per cent. ash in original sample.
B = per cent. ash in dry felt.
C = per cent. dry felt in original sample.
$A - CB$ = mineral matter in coating.
$100 - C + A - CB$ = bitumen.

(4) Ignite extracted 3-in. square and calculate per cent. ash in dry felt.

(5) Measure thickness of extracted 6-in. square felt.

(6) Make four tests on Mullen machine for strength of dry (extracted) felt. Report average.

(7) Treat 1 grm. of extracted felt with 100 c.c. of 2% sodium hydroxide in a 200 c.c. Erlenmeyer flask with reflux condenser and boil gently for ½ hour.

Filter in a Gooch crucible, washing with hot water, return fibres to flask and treat once more as above. After washing thoroughly with hot water, dry at 212° F. and weigh. Report per cent. dry felt (wool and hair)removed by 2% sodium hydroxide.

(8) Place 2 in. × 6 in. strip in ice water at 41° F. and after 15 minutes work over rods ¾ in., ⅝ in., ½ in., ⅜ in., ¼ in., and 180° flat, reporting the diameter of rod over which roofing cracks.

Weight 3 in. square in grams × 16.896 = pounds per 480 sq. ft.

Separation of Natural and Petroleum Asphalt.—Marcusson has recommended the estimation of the oil content as a means of distinguishing between natural and petroleum asphalt, since natural asphalt contains 2–34% oil, practically free from paraffin wax, while petroleum asphalt contains 26–58% oil, very rich in paraffin wax. H. Loebell (*Chem. Zeit.*, **36**, 22–23) has objected that this method is impracticable in the case of paving asphalts where small amounts of petroleum asphalt are added to Trinidad asphalt as a flux and serve to increase the percentage of oily constituents. Marcusson (*Chem. Zeit.*, **36,** 801–803) replies that this fact in itself would be sufficient to show the presence of petroleum asphaltin the natural product and cites numerous examples in support of this contention. Loebell recommends the determination of the paraffin content of the oily portion of the asphalt as a method of distinguishing between natural and petroleum asphalts, the oil from the latter being high in paraffin, but Marcusson points out that certain Roumanian petroleums show a very low paraffin content. The distillation of the asphalts, however, and determination of the acid number of the distillates are of considerable value. Distillates from petroleum asphalts have low acid numbers and free paraffin frequently separates. Natural asphalt distillates have higher acid numbers and show no free paraffin. Determination of the saponification number of the asphalt is also valuable, since this number of natural asphalts runs much higher than that of the petroleum asphalts, 28.5–34 for the former as against 7.6–13.5 for the latter. Of the petroleum asphalts, the Californian and Roumanian products have the highest saponification number. Determination of the sulphur content of asphalts is of little value since the sulphur content of certain petroleum asphalts is as high as or higher than that of some natural asphalts.

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[1] Methods of the N. Y. Testing Laboratory.

The Estimation of Natural Asphalt in the Presence of Artificial Asphalt.—Marcusson's method (*Z. angew. Chem.*, **26,** 91–93) is based on the precipitation of sulphonated bitumens from water solution. 10 grm. of material are shaken with 75 c.c. of an ether solution of hydrochloric acid (prepared by shaking ether with conc. hydrochloric acid, keeping the mixture cold) in three or four portions. After 10 minutes 75 c.c. of water are added and the mixture heated on the steam-bath until no more odour of ether is noticeable. The insoluble matter is filtered off, dried and extracted with boiling chloroform; the extract is weighed after distilling off the chloroform and drying at 105°. Three grm. of this bitumen are then treated with 6 c.c. of conc. sulphuric acid and heated on the steam-bath for 45 minutes. The product is treated with 200 c.c. of water. A precipitate settles out which, after 1 hour, is filtered off, washed free from acid, dried and weighed. This product is the natural asphalt bitumen. The amount of mineral matter in natural asphalt varies enormously, but the valuation of the material is based on its bitumen content. The results are about 4% low. Adding a correction of 4% to results obtained with Trinidad asphalt and coal-tar pitch mixtures, of known composition, gave figures fairly close to the theoretical. Petroleum residues react like natural asphalts with sulphuric acid, so that it is necessary to examine the insoluble precipitate for the paraffin content of the oily portion and the acid content of the distillate.

Estimation of the Asphalt Content of Mineral Oils, Petroleum Pitch and Similar Materials.—A series of experiments by Schwarz, (*Chem. Zeit.*, **35**, 1417) using butanone instead of acetone as prescribed in the official German methods are here given. Butanone is a good solvent for mineral oil distillates and is used in somewhat the same manner for their separation as acetone; the ready solubility of light mineral oils in butanone renders it advantageous in separating asphalt from dark mineral oils. On treating asphaltic mineral oils at room temperature with the solvent, large amounts of light oil are dissolved, whilst black, very viscous to soft pitchy masses, according to the nature of the material, remain undissolved; a sharp separation of the asphalt from the oil could not be obtained by this treatment, but on heating the butanone to boiling (81°), clear dark solutions were obtained. Butanone has the power of absorbing a significant amount of water, causing a lowering of solvent power and a more perfect separation of asphaltic substances. 1,000 c.c. of butanone at room temperature requires about 110 c.c. of water for saturation; at 20° the water-free material has sp. gr. = 0.805, saturated with water = 0.835. Tests were made on cylinder oils using a butanone-water mixture of sp. gr. 0.835 and of 0.812, the latter dissolving all oils and giving a clean, sharp separation from asphaltic matter. Estimations were made for comparison by using alcohol-ether and normal benzine. Results by the butanone and the alcohol-ether methods with some samples agreed very well, but with others there was a variation due to the nature of the asphaltic matter, soft asphaltic substances being dissolved in greater amount by the latter and hard substances less by the former. With normal benzine, the results showed that with increasing content of butanone-insoluble asphalt, there was increase in the precipitate by benzine, with a darker colouring of the benzine solution; larger amounts of asphalt are precipitated with butanone than with benzine. Experiments were made on solid bitumens

(Trinidad asphalt, soft Italian asphalt, Galician). Butanone is superior to the usual solvents for separating asphaltene from petrolene in that no chemical change is liable to take place in the constituents from overheating, and because the solvent power may be varied by varying additions of water; this makes it possible to separate the asphalt into a series of characteristic constituents. An accurate study of the latter should contribute to the knowledge of the chemical nature of asphalts and the rôle of sulphur in their formation and properties. Water-free butanone is recommended as a substitute for alcohol-ether in the determination in oils; a single precipitation (cooling of the butanone solution in ice-salt mixture and filtration at 15°) separates total paraffin wax.

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NAPHTHALENE AND ITS DERIVATIVES

BY W. A. DAVIS, B. Sc., A. C. G. I.

NAPHTHALENE, $C_{10}H_8$

Naphthalene is formed when a large number of organic compounds (*e. g.*, methane, ethylene, acetylene, acetic acid) are subjected to a red heat in the absence of oxygen. It therefore occurs in coal-tar, which is the sole source from which it is obtained on the large scale.[1] It forms 5 to 10% by weight of the crude tar; a good "middle oil" (b. p. 180° to 230°) should contain at least 30% of naphthalene. Crude naphthalene crystallises from the middle oil on standing and is purified by distillation with steam and subsequent sublimation. On the small scale, for laboratory purposes, the sublimed or steamed naphthalene can be further purified by crystallisation from hot alcohol.

Naphthalene is employed principally in the manufacture of its substitution derivatives (sulphonic acids, naphthols, naphthylamines) which are used in the dyeing industry, and in making phthalic acid (for synthetic indigo, eosin dyes), this being formed by the oxidation of naphthalene by hot fuming sulphuric acid in presence of traces of mercury sulphate. Naphthalene is also used for enriching coal-gas (albocarbon) and as an antiseptic and preservative for woollen goods.

Physical Properties.—Naphthalene crystallises in colourless orthorhombic plates, m. p. 79°, b. p. 218°, sp. gr. (solid) 1.145 at 4°, (liquid) 0.978 at 79.2°. It is practically insoluble in cold and very slightly soluble in hot water; very soluble in boiling alcohol, much less so in cold alcohol (1 in 19 parts of alcohol at 15°). It dissolves very readily in cold chloroform, carbon disulphide, benzene, light petroleum, and phenol. Melted naphthalene dissolves sulphur, phosphorus, and indigo.

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[1] In the United States it is obtained from carburetted water-gas tar. Amer. Ed.

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NAPHTHALENE, $C_{10}H_8$

Naphthalene is formed when a large number of organic compounds (*e. g.*, methane, ethylene, acetylene, acetic acid) are subjected to a red heat in the absence of oxygen. It therefore occurs in coal-tar, which is the sole source from which it is obtained on the large scale.[1] It forms 5 to 10% by weight of the crude tar; a good "middle oil" (b. p. 180° to 230°) should contain at least 30% of naphthalene. Crude naphthalene crystallises from the middle oil on standing and is purified by distillation with steam and subsequent sublimation. On the small scale, for laboratory purposes, the sublimed or steamed naphthalene can be further purified by crystallisation from hot alcohol.

Naphthalene is employed principally in the manufacture of its substitution derivatives (sulphonic acids, naphthols, naphthylamines) which are used in the dyeing industry, and in making phthalic acid (for synthetic indigo, eosin dyes), this being formed by the oxidation of naphthalene by hot fuming sulphuric acid in presence of traces of mercury sulphate. Naphthalene is also used for enriching coal-gas (albocarbon) and as an antiseptic and preservative for woollen goods.

Physical Properties.—Naphthalene crystallises in colourless orthorhombic plates, m. p. 79°, b. p. 218°, sp. gr. (solid) 1.145 at 4°, (liquid) 0.978 at 79.2°. It is practically insoluble in cold and very slightly soluble in hot water; very soluble in boiling alcohol, much less so in cold alcohol (1 in 19 parts of alcohol at 15°). It dissolves very readily in cold chloroform, carbon disulphide, benzene, light petroleum, and phenol. Melted naphthalene dissolves sulphur, phosphorus, and indigo.

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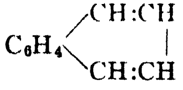
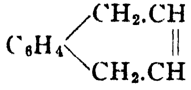
[1] In the United States it is obtained from carburetted water-gas tar. Amer. Ed.

Chemical Properties.—With picric acid naphthalene combines to form a crystalline additive compound, $C_{10}H_8$, $C_6H_2(NO_2)_3OH$, m. p. 149°; this fact is utilised in estimating naphthalene (*vide infra*). Concentrated nitric acid converts naphthalene (best when dissolved in glacial acetic acid) mainly into 1-nitronaphthalene; when an excess of acid is used at higher temperatures, various di-, tri-, and tetranitronaphthalenes are formed, according to the conditions. Concentrated sulphuric acid converts naphthalene into either the 1- or 2-sulphonic acid. The former is produced at a low temperature (80°), the latter at a high temperature (160°), best in presence of an excess of sulphuric acid. Prolonged heating with fuming sulphuric acid gives a mixture of the 2:6- and 2:7-disulphonic acids. When naphthalene is heated with fuming sulphuric acid in presence of a catalyst (mercury) phthalic acid is formed: this action is utilised on the large scale. Chromic acid in acetic acid solution converts naphthalene into 1:2-naphthaquinone. Chlorine and bromine form various substituted chloro- and bromonaphthalenes. Nascent hydrogen reduces naphthalene to dihydronaphthalene, $C_{10}H_{10}$ (sodium in ethyl alcohol), or tetrahydronaphthalene, $C_{10}H_{12}$ (sodium in amyl alcohol). Corresponding with these reduced naphthalenes are naphthalene dichloride, $C_{10}H_8Cl_2$ (prepared from naphthalene by means of potassium chlorate and hydrochloric acid), and naphthalene tetrachloride (formed on passing chlorine into a chloroform solution of naphthalene). The following formulæ show the relationship between these compounds.



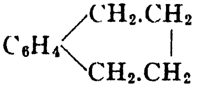
$$C_6H_4{<}\begin{matrix}CH:CH\\ |\\ CH:CH\end{matrix}$$

Naphthalene



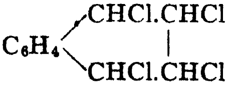
$$C_6H_4{<}\begin{matrix}CH_2.CH\\ \|\\ CH_2.CH\end{matrix}$$

Dihydronaphthalene



$$C_6H_4{<}\begin{matrix}CH_2.CH_2\\ |\\ CH_2.CH_2\end{matrix}$$

Tetrahydronaphthalene



$$C_6H_4{<}\begin{matrix}CHCl.CHCl\\ |\\ CHCl.CHCl\end{matrix}$$

Naphthalene tetrachloride

The hydrogenated naphthalenes have recently become of technical importance in the form of the "tetralin" compounds of the Tetralin Gesellschaft. For these hydrogenated compounds see Schroetter and others (*Annalen*, 1922, **426**, 1–17, 17–83, 83–160). "*Tetralin*" (*tetrahydronaphthalene*) has a sp. gr. at 20°/4° of 0.971; $n_D^{20^\circ}$ 1.5434,

b. p. 100–101 under 25 mm. and 206.5° under 75 mm. *Decahydronaphthalene* has sp. gr. 18°/4° = 0.8842; b. p. 189–191° under 770 mm.

For a review of the hydrogenation of hydrocarbons see *J. Soc. Chem. Ind.*, 1921, 445R. Rowe, *ibid.*, 1921, 588, and patents of the *Tetralin Gesellschaft*, 1920 onwards.

For a systematic review and bibliography of naphthalene derivatives see Reverdin and Fulda's *Tabellarische Uebersicht der Naphthalinderivate* and the Reports of the *Committee on Isomeric Naphthalene Derivatives* of the British Association.

Detection of Naphthalene.—To detect naphthalene in a material thought to contain it (the characteristic smell of naphthalene is a useful index of its presence) the substance is subjected to distillation in a current of steam and the distillate made alkaline with sodium hydroxide to remove phenols; if naphthalene is present it remains undissolved in a state of greater or less purity. It is characterised by re-steaming (if necessary) or crystallising from alcohol, the m. p., characteristic smell, and property of forming a well-defined picrate serving to identify the final product.

Estimation of Naphthalene:

A. *In Coal-gas.*

Small quantities of naphthalene are usually present in coal-gas. In cold weather this may crystallise out and cause obstruction in the pipes. The proportion of naphthalene present in the gas is generally estimated by a modification of Colman and Smith's method (*J. Soc. Chem. Ind.*, 1900, **19**, 128). This depends on the formation of an additive compound of naphthalene with picric acid which is insoluble in dilute aqueous picric acid. The solution of picric acid used is one which is nearly saturated with picric acid at the ordinary temperature (roughly N/20): it is standardised by titration with N/10 barium hydroxide or sodium hydroxide, using lacmoid as indicator.

Several modifications have been suggested for this estimation, of which the following are the most recent.

According to H. G. Colman's latest description (*Gas J.*, 1918, **144**, 231–232) the gas (about 10 cu. ft.) is passed at a rate not exceeding 1 cu. ft. per hour (the volume being corrected to 60° F. and 30° pressure) through a series of four wash bottles, of glass throughout.

1. Contains a 10% solution of citric acid to retain any ammonia;
2. Contains 100 c.c. of N/20 picric acid;
3. Contains 50 c.c. of the same solution;
4. Is left empty to retain spray.

The gas must not come in contact with India rubber during or prior to its passage through the train. When the passage of the gas is terminated the contents of bottles (3) and (4) are washed into bottle (2), which is then closed with a tight-fitting rubber stopper furnished with a glass stopcock. The wash bottle is evacuated until the naphthalene picrate rises to the surface, the stopcock is then closed and the contents of the bottle heated to boiling, with occasional shaking. The contents are then corked, shaking from time to time, the volume of the mixture carefully measured, and the naphthalene picrate separated by filtration through a dry filter paper, the first few c.c. of the filtrate being rejected. 100 c.c. of the filtrate is then titrated into N/10 sodium hydroxide using lacmoid or phenol phthalein as indicator. The N/20 picric acid used for the aborption has previously been standardised in the same manner. If v represents the difference of volume of N/10 alkali required to neutralise the total volume of N/20 picric acid taken and that required to neutralise the same volume after the heating and filtering, then

$$\text{grains naphthalene per 100 cu. ft.} = \frac{v \times 19.75}{\text{vol. of gas passed}}.$$

Knublauch (*J. Gasbeleucht.*, 1916, Oct. 14 and 21) recommends the following procedure: a sufficient volume of the gas to give about 0.08 grm. of naphthalene is passed at the rate of 50–55 litres an hour through two wash bottles containing 110 c.c. and 25 c.c. respectively of 1% picric acid. If much ammonia is present, the first bottle is charged into a mixture of 40 c.c. of the picric acid solution, 40 c.c. of N/1 sulphuric acid and 30 c.c. water. The precipitated picrate is filtered off, a 0.2% solution of picric acid being used for washing: 100 c.c. of this should suffice even when sulphuric acid is present. Any particles of picrate remaining in the second bottle are washed with a little water into the first, to which is also transferred the filter and precipitate. Methyl orange is added and the contents titrated with N/10 alkali. In titrating, a deduction (0.1 c.c. for an 8 cm. filter paper) is made for the picric acid absorbed by the filter paper. The result × 0.0128 gives the weight of naphthalene.

A. Wein (*J. Gasbeleucht.*, 1911, **54**, 891) and Schlumberger have suggested methods in which the naphthalene is precipitated as picrate in a similar manner but the picric acid solution is titrated before and after the action by means of the iodine liberated from a mixture of potassium iodate and iodide, according to the equation

$$KIO_3 + 5KI + 6C_6H_2(NO_2)_3.OH = 6C_6H_2(NO_2)_3.OK + 3H_2O + 6I.$$

Dickenson Gair (*J. Soc. Chem. Ind.*, 1905, **24**, 1279 and 1907, **26**, 1263) has suggested an alternative method to avoid heating and re-precipitating the solution of naphthalene picrate. The naphthalene is absorbed from the coal-gas by passing it through acetic acid of sp. gr. 1.044. Picric acid is then added in excess, which causes an immediate precipitation of fine naphthalene picrate. This can be collected and weighed, or can be dealt with volumetrically when rapidity is an important consideration.

B. *In Spent Oxide of Iron.* In Gair's method (*loc. cit.*) 10 grm. of the undried oxide, roughly powdered, are extracted in a small flask with 100 c.c. of 80% alcohol, by shaking well and leaving it to stand for 3 or 4 hours. The liquid is filtered into a larger flask and the paper washed once or twice with dilute alcohol. 300 c.c. of strong picric acid solution are added, the flask is well agitated, and the mixture allowed to stand for a short time. The naphthalene picrate which separates can be weighed or dealt with volumetrically as above.

According to W. C. Davis (*J. Soc. Chem. Ind.*, 1914, **33**, 1120) 10 grm. of the sample are weighed into a Wurtz flask and subjected to distillation in steam, which is passed through a second Wurtz flask heated at 100° and containing 50 c.c. of N-sulphuric acid or citric acid, then into a condenser and finally into a receiver consisting of a wide-mouthed bottle. The whole apparatus is sealed by placing at the exit a wash bottle containing 25 c.c. of saturated picric acid. The distillation is complete in about 10 minutes. The naphthalene in the condenser is then melted out, the picric acid in the final washing flask is washed into the receiver and sufficient solid picric acid added to make the whole solution saturated. The receiver is closed with a rubber stopper and heated in a water bath until a clear solution is obtained. The solution is cooled, shaking occasionally, and the excess of picric acid estimated by titrating with N/10 sodium hydroxide in the usual manner. Experiments made with known weights of pure naphthalene showed this process to be sufficiently accurate for all practical purposes.

C. *Estimation of Naphthalene in Middle Oil and Carbolic Oil.* The middle oil is first melted, if necessary, and thoroughly mixed. A weighed quantity (500 to 2,000 grm.) is then left during 24 hours to crystallise, being well stirred at frequent intervals. The crystals which separate are collected by the aid of a vacuum filter, pressed completely free from oil in a small press, and weighed. The b. p. of the naphthalene should be determined by distilling 100 grm. of the pressed crystals and collecting and weighing the various fractions passing over at different temperatures. A good middle oil should contain not less than 30% of naphthalene boiling between 210° and 220°.

The naphthalene in carbolic oil can be estimated by removing the phenols by extracting with aqueous sodium hydroxide, washing the residue with water and allowing the naphthalene to separate from the residual oil as in the case of middle oil.

D. *In Phenol.*

The presence of naphthalene in phenol is shown by dissolving away the phenol with dilute aqueous sodium hydroxide: the naphthalene remains undissolved. To estimate the naphthalene in this case the residue obtained is extracted with ether, the ether being then evaporated and the naphthalene weighed, either as such or in the form of its picrate (see above).

For the estimation of naphthalene in tar and tar oil Mezger (*Gas und Wasserfach.*, 1921, **64**, 413) gives the following method: a current of purified coal gas is passed through a flask containing a suitable weight of the material (*viz.*, 0.4–0.8 grm. of tar oil, 0.1 to 0.2 grm. crude naphthalene, or 0.5 to 1.0 grm. tar) with 5 c.c. of 15% phosphoric acid. The issuing gas is led into a potash bulb filled with potash solution (1:1), the flask and bulb being supported in a vessel of water maintained at 65–70°. The naphthalene is collected in a scrubber consisting of a reservoir with a bulb-tube sloping upwards from the bottom of the reservoir, and containing 50 c.c. of saturated picric acid. The gas is passed at 25 litres per hour and extraction contained during 3½ hours. The contents of the scrubber are then filtered, the scrubber and filter washed with water and the washings added to the filtrate and the whole is then titrated with N/10 sodium hydroxide using sodium alizarin sulphonate as indicator. A correction is made for the volume of the filtrate adhering to the filter paper and precipitate.

Hydrogen gas can with advantage be used to replace coal gas as volatilising agent (see Hofsäss, Herrmann and Mezger (*Gas und Wasserfach.*, 1921, **64**, 722–723). Homologues of naphthalene, *e. g.* acenaphthene, phenanthrene and chrysene are also volatilised under the above conditions but their amounts in commercial products are usually negligible. It is doubtful whether the amount of phosphoric acid would retain all the bases present in highly basic fractions of tar. The time (3½ hours) can often be considerably reduced, as the disappearance of the deposit of naphthalene formed at first on the dry bulb marks the end of the action. With slight modifications the method should be suitable for adoption as a standard method of analysis.

E. *Estimation of Naphthalene in Pesticides.*

Owing to the volatility of naphthalene, this substance is difficult to estimate by simple methods. S. H. Collins (*J. Soc. Chem. Ind.*, 1918, **37**, 131R) extracts the naphthalene by a solvent prepared by distilling methylated ether at 27–33°. If not more than one-half of the solvent is recovered and the rest expelled with a current of air, no loss of naphthalene occurs. The residue can be dried in two days without loss of naphthalene in a desiccator containing equal parts of fused calcium chloride and naphthalene balls, the object of the latter being to saturate the atmosphere with naphthalene vapours and to absorb the ether.

Commercial Naphthalene

Naphthalene is contained largely in the less volatile portions of coal-tar naphtha, in the crude carbolic acid and "creosote oils" which subsequently distil, and in the semi-fluid "anthracene oils" obtained at a still higher temperature. By cooling the portion of the coal-tar distillate which passes over about 200°, naphthalene is frequently deposited in such quantities as to render the product semi-solid. It may be separated by pressure from the liquid oils, and purified by heating strongly with 5 to 10% of concentrated sulphuric acid, washing thoroughly with water, and subliming the product.

Naphthalene is now prepared commercially of high purity as colourless crystals which distil wholly within a very few degrees of the b. p.

of pure naphthalene, and give no pink colour with sulphuric acid. Besides this nearly pure product, which, when remelted and cast into moulds, is employed as "albocarbon," and (under the name "coal-tar camphor") for protecting furs and woollens from moths, naphthalene occurs in commerce as an impure, coarsely crystalline substance of rank odour, technically known as crude naphthalene or "naphthalene salts."

Crude Naphthalene

To ascertain the quality of "naphthalene salts" an average sample of several kilograms is melted in a dish on the water-bath and thoroughly mixed. 15 to 20 grm. of the liquid are poured into a mortar and, after solidifying, broken into powder. 10 grm. are weighed on to filter-paper which is carefully folded over it, the whole being then enclosed in a piece of linen. The mass is then pressed in a small hydraulic press under a pressure of 200 atm. or in a vice till no more oil squeezes out. The solid cake is again powdered, the pressing being again repeated as before. The final cake obtained is weighed. A good sample should not contain more than 10 to 12% of oil.

The proportion of higher hydrocarbons in the pressed cake is ascertained by distilling about 100 grm. (prepared as above) from a retort, the neck of which is kept warm so as to prevent it from becoming choked. A good sample of pressed "salts" should yield nothing below 210°, and 90% should distil before 225° is reached.

The sublimed naphthalene of commerce contains 70 to 100% of the pure substance. The finer qualities form colourless crystals, but the inferior grades have a fawn or brown colour. A good test for the purity of sublimed naphthalene is to warm the sample in a test-tube with a little pure concentrated sulphuric acid. Pure naphthalene produces a colourless solution, but a decided pinkish tint is observed if as little as 1% of impurity is present. The coloration becomes deeper pink, or even brown, when a greater proportion of foreign matters is present.

The m. p. is always taken wet, as the difference between the m. p. of dry naphthalene and that containing a small amount of water is considerable, but the difference between that containing 4% of water and an amount in excess of this by several per cent. is inappreciable. So, unless it is known that the crude naphthalene contains as much as 4% of water, that much is added before taking the m. p.

The test is made after adding water in large brass or glass test-tubes, holding several ounces. The sample is melted and the point is noted when, on cooling, the temperature becomes constant after it has been rising. High m. p. naphthalenes show this constant temperature for quite a while. With low m. p. samples the point is not so sharply defined, as the temperature does not remain constant very long. Those not accustomed to making this test should that repeat it until they feel sure they have caught the point at which the temperature is constant for a longer or shorter time.

The chief methods for the determination of naphthalene have heretofore depended upon a final estimation of the naphthalene by precipitation with an excess of picric acid (see p. 213) and titration of the excess with standard alkali. Such methods have been found in practice to be slow and to require extremely careful manipulation.

The following method for the analysis of naphthalene and naphthalene sulphuric acid has been proposed by Calcott, English and Downing (*Ind. Eng. Chem.*, 1924, **16**, 27–29).

Sodium Hydroxide Solution.—Boil 5% sodium hydroxide solution for about 15 minutes with an excess of refined naphthalene (5 grm. naphthalene to 1 litre caustic solution), allow the mixture to cool to room temperature, and store the solution in the presence of an excess of naphthalene. Filter the solution free from naphthalene as it is required for use.

Sulphuric Acid (10%).—Prepare a stock solution of sulphuric acid 10% by weight in strength.

Apparatus.—A convenient form of steam distillation apparatus consists of a 1 litre Florence flask as a steam generator; two 500 c.c., wide-mouthed, round-bottom flasks, rubber-stoppered, equipped with inlet tubes of 10 mm. glass tubing reaching to the bottoms of the flasks and outlet tubes of Kjeldahl bulbs as traps, a 1 litre balloon flask as receiver, containing a 10 mm. inlet tube reaching almost to the bottom of the flask, and an outlet tube leading to the bottom of an auxiliary 500 c.c. balloon flask receiver.

Place the sample, together with the naphthalene-saturated sodium hydroxide solution, in the first 500 c.c. wide-mouthed flask, place 10% sulphuric acid in the second 500 c.c. flask, run a stream of cold water over the 1 litre receiving flask, and immerse the 500 c.c. auxiliary flask in ice and water.

Procedure.—The material must be carefully sampled if consistent results are to be obtained. Place 100 to 200 grm. or the entire available sample in a large glass mortar and mix thoroughly. The sample taken should contain 8 to 10 grm. of naphthalene; therefore, a 10-grm. sample of refined naphthalene or a 12 to 15 grm. sample of crude naphthalene should be taken, depending upon the probable purity of the crude material.

Transfer the sample to the first 500 c.c. flask and add 100 c.c. of the 5% sodium hydroxide reagent. The addition of an 11 cm. No. 5 Whatman filter paper torn into small pieces is advisable, since it prevents the tar in the sample from clinging to the sides of the flask during distillation.

In the second 500 c.c. flask place 100 c.c. of 10% sulphuric acid. Place hot tap water in the steam generator, connect up the apparatus, start a stream of cold water running over the 1 litre receiver, and place the 500 c.c. receiver in a large beaker of ice and water.

Steam-distil the sample, heating the sample and sulphuric acid flasks meanwhile to maintain the volumes of solution constant. After steam-distilling for approximately 20 minutes, the distillation should be interrupted and the 1 litre receiving flask replaced with a clean one. Continue the distillation, observing the nature of the product separating in the receiver. The distillation is complete when nothing but oil (frequently yellow) separates in the receiver, or the receiving flask fills with a white fog of acrid-smelling vapour. The distillation usually requires three receiving flasks and is complete in 45 to 60 minutes.

Wash the naphthalene from the receiving flasks, tubing and auxiliary flask on to a 10 cm. (4-in.) Büchner funnel containing two thicknesses of filter paper. Final traces of naphthalene in the receivers may be removed by draining them free of water and then dissolving the naphthalene in 95% alcohol. Not over 10 c.c. of alcohol should be used for this purpose, since some is retained by the naphthalene and later interferes with the sulphonation. Dilute the alcohol washings with 150 to 200 c.c. of distilled water and filter through the Büchner funnel. Transfer the bulk of the naphthalene from the funnel to a 400 c.c. beaker and thoroughly crush the lumps. Finally, rinse the funnel and filter paper free from naphthalene with distilled water. Again filter the naphthalene, this time upon a large (35 c.c.) Gooch crucible containing a disk of filter paper, press the cake with a rubber stopper and suck as dry as possible.

Transfer the naphthalene to a heavy-walled Pyrex test tube (3 cm. inside diameter × 16 cm. in height, capacity 110 c.c.), add 25 c.c. of C. P. concentrated sulphuric acid, then 30 c.c. of 20% "oleum." Stopper the tube tightly with a rubber stopper, stand upright in a bath of boiling water reaching almost to the rim of the tube, and sulphonate for 1 hour at 100°, removing the tube at intervals of 10 minutes and mixing the contents as thoroughly as possible without splashing the acid upon the rubber stopper. Cool the tube and dilute the contents in 250 c.c. of cold water. Boil for 15 to 20 minutes to remove any sulphur dioxide or volatile unsulphonated oil present, cool to room temperature, and dilute to 1 liter in a volumetric flask.

Oxidise 25 c.c. aliquots with vanadic acid. Dilute in each case to 500 c.c. and titrate 75 c.c. aliquots with N/10 potassium permanganate solution.

Calculation.—

$$\frac{(\text{c.c. KMnO}_4 - \text{blank}) \times \text{normality of KMnO}_4 \times 0.7117}{\text{Weight of sample in aliquot}} = \text{per cent. naphthalene.}$$

Discussion of the Analytical Procedure.—The constituents of crude naphthalene are not entirely known, but the material, as crystals pressed from the carbolic fraction of coal tar, is known to contain phenols and cresols, some quinoline bases, and a certain amount of easily oxidisable material which persists in the purified material and is detected by the wash test with concentrated sulphuric acid. In the procedure adopted for the crude material, the steam distillation from dilute sodium hydroxide removes phenolic impurities, the 10% sulphuric acid retains volatile basic impurities, whilst the bulk of the tar is nonvolatile and remains as residue in the apparatus.

Of material other than naphthalene which distils over, the aliphatic impurities would be largely unaffected by the sulphonation treatment and would be volatilised in the boiling to ensure elimination of any sulphur dioxide after sulphonation, whilst the easily oxidisable impurities are probably oxidised by the oleum in the sulphonation.

Naphthalene cannot be quantitatively steam-distilled from sodium hydroxide solution; so for this reason sodium hydroxide saturated with naphthalene is used in the distillation procedure.

Water and so-called available naphthalene are estimated by distillation. 10 grm. are weighed into a small copper still connected with a condenser, a little heavy coal-tar naphtha (free from tar) is added and distillation begun. The distillation is carried to 205° (for carrying over water) with a water condenser and then it is completed with an air condenser. The distillation is carried to dryness. The residue left in the still is tarry matter and dirt. The percentage of water is added to this figure and the combined amount deducted from the amount of the original crude naphthalene taken, the balance being naphthalene available for refining. This is not all flake naphthalene as there is some oil present.

For some uses anhydrous naphthalene is desirable, or an accurate knowledge of its water content is essential (Calcott, English and Downing, *Ind. Eng. Chem.* 1924, **16**, 29–30). The use of the freezing point as a criterion of quality may give erroneous results due to the presence of an unknown percentage of water. For these reasons a rapid and accurate method for the estimation of small amounts of water in naphthalene has been suggested. The method is chiefly adapted to sublimed naphthalene, but in certain cases it may be applied to products of lower purity.

The estimation depends upon the fact that toluene is capable of dissolving water in amounts which are small but which increase rapidly with rising temperatures. Such a solution when cooled remains clear until a certain temperature is reached and then becomes milky owing to the separation of fine droplets of water. The so-called critical solution temperature obtained in this manner is sharply defined, closely reproducible, and, since it was found to be unaffected by low concentrations of naphthalene in the toluene, admirably served the purpose of the investigators.

Estimation of Water. *Apparatus.*—The apparatus consists of a flat-bottomed flask, the body of which is 3 cm. in diameter and 5 cm. high and has a volume of 25 to 30 c.c. The neck is approximately 5 cm. long and 1.5 cm. in diameter, and has a constricted portion 2 cm. long which is just above the body of the flask and designed to fit snugly around a 100° thermometer. A 20 c.c. pipette, having a calcium chloride tube attached to the mouthpiece, is used to add the toluene to the apparatus. The calcium chloride tube serves to remove any moisture which might be drawn in as the pipette is emptied.

Standard Toluene-water Solution.—A standard solution of water in toluene having a critical temperature of 20° ± 5° is used as solvent for the sample. Add 4 drops of water to 1 litre of freshly distilled C. P. toluene, heat the solution to 40°, shake vigorously, and allow to stand 24 hours. If a cloud appears, it is necessary to add more water-free toluene and repeat the heating and shaking. When a solution is obtained which is clear at room temperature, place a portion in the apparatus and determine its critical solution temperature. If a temperature between 20° and 25° is obtained, add water-free toluene to the stock reagent until the critical temperature becomes 20° ± 5°. Always shake the reagent before using, since water, having a higher vapour pressure than toluene, tends to condense on the walls of the bottle above the surface of the liquid.

Procedure.—Weigh accurately about 2 grm. of naphthalene into the apparatus and add 20 c.c. of the standard toluene-water mixture. Cork the apparatus, heat to 50° to 60°, and shake thoroughly. Insert the thermometer, and shake the apparatus while it is cooling in the air until an incipient milkiness appears. Note the temperature and continue shaking until the temperature drops another half degree to confirm the reading first taken. The table (see p. 224) gives the weight of water in grams corresponding to various critical solution temperatures.

The table gives directly the grm. water in the sample, based upon a standard toluene reagent of an initial temperature 20°.

$$\frac{\text{Wt. of water from table} \times 100}{\text{Sample weight}} = \text{per cent. moisture.}$$

Refined naphthalene is valued by colour, m. p., a sulphuric acid test, and sometimes by distillation. The m. p. of naphthalene is generally between 78° and 78.5° (wet) and sometimes as high as 79°. Good results are not usually obtainable when the m. p. is so low as 78°.

The **sulphuric acid** test is a fairly sure indication of the keeping qualities as regards colour. The sample is melted and agitated with ⅓ volume of concentrated sulphuric acid for a short time. The naphthalene should remain white when first cooled. On re-melting

DETERMINATION OF MOISTURE IN NAPHTHALENE

Critical solution temperature,° C.	Water, grm.	Critical solution temperature ° C.	Water, grm.
20	0.00000	39	0.01055
21	0.00056	40	0.01110
22	0.00111	41	0.01167
23	0.00167	42	0.01222
24	0 00222	43	0.01278
25	0.00278	44	0.01333
26	0.00333	45	0.01388
27	0.00388	46	0.01444
28	0.00444	47	0.01500
29	0.00500	48	0.01555
30	0.00555	49	0.01611
31	0.00611	50	0.01667
32	0.00667	51	0.01723
33	0.00723	52	0.01778
34	0.00778	53	0.01833
35	0.00833	54	0.01889
36	0.00889	55	0.01946
37	0 00946	56	0.01200
38	0.01000	57	0.02055

it generally becomes red. The acid is red in any case. If poorly refined the naphthalene will show yellowish to reddish, and such material would not retain its colour.

The works' tests on crude and refined naphthalenes in the United States may show some differences from English and Continental practice.[1]

Pure Naphthalene

Specially purified naphthalene is now required in chemical industry particularly in the manufacture of dyes. For this class of work naphthalene (dry) must melt sharply at 79°, boil between 217° and 218°, and be practically odourless; it must dissolve completely in light petroleum, giving a transparent, colourless solution. The monosulphonic acid prepared from it should not show a greyish tinge and the sodium salt of the acid must be snow-white. Naphthalene which answers these requirements does not become yellow when exposed to air and light, and when dissolved in concentrated colourless sulphuric acid gives a solution with only a very faint pink colour.

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[1] The above information is supplied by Mr. John M. Weiss, New York.

The sensitiveness of naphthalene to air and light may be tested in the following way (Lunge's *Chem. Tech. Unters. Meth.*, 1905, II, 762). A sample is left in a clock glass under a bell-shade over a vessel of pure, concentrated non-fuming nitric acid, when it should not show a yellow tinge for at least 1 or 2 hours. After this time even pure naphthalene changes colour owing to its undergoing nitration on the surface.

To test for phenol in naphthalene the latter is extracted with dilute sodium hydroxide solution, excess of hydrochloric acid added to the extract, and, after filtering, bromine water. Tribromophenol separates if phenol is present.

Basic substances are seldom found in naphthalene, but they can be detected, if present, by extracting with sulphuric acid, adding an excess of alkali and distilling with steam. The bases are recognised by their characteristic odour.

To estimate the percentage of naphthalene in a commercial product Küster (*Ber.*, 1894, **27**, 1101) devised the method of precipitation with picric acid. The procedure is that described on pages 213 and 215. The picrate may be either weighed or estimated volumetrically, using an excess of picric acid and titrating back. It is essential in this method that other hydrocarbons which form insoluble picrates should be absent.

NAPHTHALENE OILS

This name, as also that of "creosote oil," is applied to the fraction of coal-tar distilling between 200° and 280° or 300°. Its composition is very imperfectly understood, but besides phenols and phenolic substances and a variety of bases, it is apparently largely composed of naphthalene and certain hydrides and homologues of that compound, the following of which have been described as being present.

Naphthalene dihydride, $C_{10}H_8H_2$, is a viscid liquid of strong, disagreeable smell, boiling at 200° to 210°. It is powerfully acted on by bromine, and is soluble in cold fuming nitric acid.

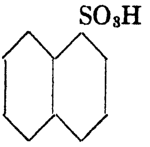
Naphthalene tetrahydride, $C_{10}H_8H_4$, resembles the dihydride, but boils at 190°.

α- and β-Methylnaphthalenes, $C_{10}H_7CH_3$, occur in the fraction of coal-tar distilling between 220° and 270° (see Wendt, *J. Pr. Chem.*, ii, 1892, **46**, 317). At the ordinary temperature the α-variety forms a colourless liquid with a blue fluorescence and pleasant aromatic odour. It has a sp. gr. 1.0005 at 19°, distils in a current of open steam, boils at 240° to 243°, and crystallises at −22° to a hard mass. The *picrate* melts at 115.5°. α-Methylnaphthalene is miscible in all proportions with alcohol, ether, glacial acetic acid, carbon disulphide, and benzene. It is readily attacked by oxidising agents. β-Methylnaphthalene crystallises, like naphthalene, in large white plates, melts at 32.5°, and boils at 241 to 242°. Regarding the occurrence of α- and β-methylnaphthalenes in paraffin (Erdöl), see Tammann, D. R. P., 95579.

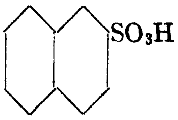
Dimethylnaphthalenes, $C_{10}H_6(CH_3)_2$. According to Emmer, and Reingruber (*Annalen*, 1882, **211**, 365), the fraction of coal-tar boiling between 252° and 270°—after removing basic, oxygenated and crystallisable substances—apparently consists of a mixture of several isomeric dimethylnaphthalenes, the separation of which has hitherto proved unmanageable. These compounds are said to constitute the major portion of coal-tar creosote oils.

The analysis of naphthalene oils is described in the section on "Creosote Oils."

NAPHTHALENESULPHONIC ACIDS



α-Naphthalenesulphonic acid.



β-Naphthalenesulphonic acid.

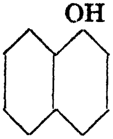
When naphthalene is heated with concentrated sulphuric acid α- and β-naphthalenesulphonic acids are formed. At low temperatures (80°) the α-acid is the principal product, but at higher temperatures (160° to 170°), and especially when an excess of sulphuric acid is present, the β-acid predominates. When the α-acid is heated with concentrated sulphuric acid it is converted into the β-acid. Both acids are deliquescent, crystalline substances. They can be separated by the crystallisation of their calcium or lead salts, the α-salt having a very different solubility from that of the β-salt.

Differences:

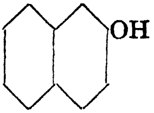
α-Acid	β-Acid
Heated with hydrochloric acid at 200° gives naphthalene and sulphuric acid..........	Heated with hydrochloric acid at 200° is not decomposed.
Sulphochloride, m. p. 66°, b. p. 195° (13 mm.).	Sulphochloride, m. p. 76°, b. p. 201° (13 mm.).
Sulphonamide, m. p. 150°..............	Sulphonamide, m. p. 212° (217° Corr.).

Numerous naphthalenedisulphonic and trisulphonic acids are known; for references see Reverdin and Fulda's *Tabellarische Uebersicht.*

NAPHTHOLS



α-Naphthol.



β-Naphthol.

α- and β-naphthols (1- and 2-hydroxynaphthalenes) are prepared by fusing the corresponding α- and β-naphthalenesulphonic acids or their sodium salts with sodium hydroxide and subsequently liberating by dilute acid the naphthols from the sodium salts thus formed. They are of great importance in chemical industry as the starting-point from which a large number of important dyes are prepared. Both naphthols have been found in the "green oils" left after the filtration of the anthracene from a high boiling fraction of coal-tar (Schulze, *Annalen*, 1885, **227**, 143).

The naphthols are sparingly soluble in hot water (the α-compound less than the β-form) and nearly insoluble in cold water. They are easily soluble in most of the usual organic solvents. α-naphthol is far more volatile with steam than β-naphthol. Both naphthols—like phenols in general—are readily soluble in aqueous sodium hydroxide, forming sodium naphthoxides, which are decomposed by carbon dioxide, the parent naphthols being liberated. Aqueous solutions of the naphthoxides on concentration undergo partial decomposition in the same manner. α- and β-naphthols are not soluble in solutions of alkali carbonates, but the nitronaphthols which are more acid in character, liberate carbon dioxide from carbonates forming salts analogous to the picrates.

With sulphuric acid the naphthols combine to form an important series of sulphonic acids. Nitric acid does not nitrate the naphthols in a simple manner[1] so that the nitronaphthols are generally prepared by indirect methods from the nitroso-naphthols or from naphthylaminesulphonic acids (see Vol. VI). With bromine and chlorine the naphthols give a remarkable series of derivatives. The chlorine derivatives have been studied by Zincke: in this case the action is more complex than simple substitution, but with bromine simple substitution alone occurs, and a very large number of well-defined bromo-compounds can be isolated, the nature of the compound formed depending on the conditions (W. A. Davis, Reports of the British Association Committee, 1901 and 1902). Etherification is effected much more readily in the case of α- and β-naphthol than with most other phenols. On simply heating the naphthols with the corresponding alcohol and a small proportion of sulphuric acid the methyl- and ethyl-ethers are obtained in nearly theoretical proportion. The substituted naphthols etherify far less readily than the parent naphthols, in some cases not at all under the conditions named (see W. A. Davis, *Trans.*, 1900, 77, 33).

Qualitative Tests.—The analytical examination of the naphthols has become of importance in view of their value as antiseptics, disinfectants, and therapeutic agents. β-naphthol is now almost exclusively used, being regarded as the less toxic form. It is now readily obtainable in a high degree of purity. Many tests have been devised for distinguishing between the two naphthols and for detecting one in the presence of the other. The following table summarises the more trustworthy of these, as applied to the purified substances:

For distinguishing between *naphthalene*, *α-naphthol*, and *β-naphthol*, L. Reuter (*Pharm. Zeit.*, 1891, 289) utilises the difference of action of chloral hydrate and zinc. 0.1 grm. of the sample is mixed with 2.5 grm. of fused chloral hydrate and warmed during ten minutes. A similar experiment is performed with addition of 5 drops of strong hydrochloric acid, and also with the same amount of acid and a piece of zinc.

---

[1] When β-naphthol is carefully nitrated with the theoretical quantity of nitric acid in glacial acetic acid solution at 0° and the product then treated with sodium sulphite solution (to reduce the nitro keto-compound initially formed) about 50 % of the theoretical quantity of 1-nitro-2-naphthol is obtained on steaming (W. A. Davis). When α- and β-naphthols are exposed to the action of nitrogen dioxide (NO_2) and the products treated with alkalies or, better, with alkaline sulphite, mononitro-derivatives of the naphthols are obtained (Armstrong and Rossiter, Proc., 1891, 7, 91).

	α-Naphthol	β-Naphthol
Odour	Faint, resembling phenol.	Almost odourless.
Crystalline form	Monoclinic needles	Monoclinic plates.
M. p., °	94	122
B. p., °	280. Readily distils with open steam.	286. Scarcely distils with open steam.
Ferric chloride in aqueous solution.	Red, turning to violet.	Pale green.
Bleaching powder in aqueous sotion.	Dark violet, changing to reddish-brown.	Pale yellow. When excess of bleaching powder is present, the colour disappears
Azo-test, 1 c.c. of acid solution of sulphanilic acid (sulphanilic acid, 0.5 grm.; acetic acid [30%], 150 c.c.). Freshly prepared very dilute solution of sodium nitrite, a few drops added at time of making test. The colours develop slowly.	Orange-red	Yellow.
A few drops of a solution of 1 grm. of potassium dichromate and 1 grm. of nitric acid in 100 c.c. of distilled water, added to a solution of the sample in water or very dilute alcohol.	Black precipitate	No precipitate.
0.1 grm. of vanillin is dissolved in 2 c.c. sulphuric acid and 0.1 grm. of naphthol added and the mixture shaken.	Permanent red colour.	Green solution.

Jorissen (*Ann. Chim. Anal.*, 1902, 7, 217) recommends as a means of distinguishing α-naphthol from β-naphthol the following procedure: a pinch of the sample is mixed in a test-tube with 2 c.c. of a solution of iodine in potassium iodide and then with an excess of aqueous sodium hydroxide. On shaking, β-naphthol gives a clear, colourless liquid, but α-naphthol gives a turbid liquid of an intensely violet colour. In the case of a mixture the colour is proportional to the amount of α-naphthol present.

L. P. J. Palet (*Anal. Soc. Quim. Argentina; J. Soc. Chem. Ind.*, 1919, 38, 55A) gives the following as a delicate test for α-naphthol in β-naphthol. Small pieces of the root of alfalfa, which contains oxidases and peroxidases, are added to a solution of pyramidone; a violet colour is produced on the roots on standing, the appearance of colour being accelerated but not intensified by the addition of

	Naphthalene	α-Naphthol	β-Naphthol
Chloral hydrate	Colourless	Intensely ruby-red, transparent, not fluorescent.	Pure blue, transparent, not fluorescent.
Chloral hydrate, and acid.	Very slight pink.	Intensely dark greenish-blue, not transparent.	Intensely yellow, transparent.
Chloral hydrate, acid and zinc.	Violet, passing into brown.	A dark violet-blue (Water gives a violet flocculent precipitate) Alcoholic solution, reddish-violet with a violet fluorescence	Dark brown. (Water throws down a greasy ppt.) Alcoholic solution, yellow with a blue fluorescence.

hydrogen peroxide. The further addition of α-naphthol immediately produces an intense wine-red colour characteristically different from that given by β-naphthol. A. Escaich (*J. Pharm. Chim.*, 1920, **22**, 138) gives the following distinguishing tests: α-naphthol in aqueous alcoholic solution treated with sodium nitrite and a few drops of acid mercuric sulphate gives a fine red coloration and then a precipitate resembling mercuric iodide. β-naphthol gives a yellowish precipitate under the same conditions.

Commercial α-naphthol

The best means of ascertaining the degree of purity of either of the commercially pure naphthols is to take the m. p. Technical α-naphthol generally consists of crystalline lumps formed by the solidification of the fused material and melts somewhat below 94°, the m. p. of the pure naphthol, owing to the presence of small quantities of β-naphthol as an impurity. 0.5 grm. of the naphthol when ignited should not leave behind any weighable ash. As in the case of β-naphthol, α-naphthol should dissolve completely in aqueous ammonia (sp. gr. 0.96) (absence of naphthalene).

Commercial β-naphthol

Technical β-naphthol is usually a highly purified substance, and should melt at 122°. The U. S. P. requirements are that it should leave no ash and that 1 grm. should dissolve completely in 50 c.c.

of ammonia (sp. gr. 0.96) (absence of naphthalene)—the solution having only a pale yellow colour (absence of organic impurities). On shaking 1 grm. of the naphthol with 100 c.c. of water the solution should be neutral to litmus-paper (absence of organic acids). On dissolving 1 grm. of β-naphthol in boiling water (100 c.c.), filtering and adding bleaching powder, the solution should show only a pale yellow and not a violet colour (absence of α-naphthol). The B. P. of 1914 gives the following test for the absence of α-naphthol. 0.1 grm. dissolved in 10 c.c. of boiling water gives with 10 drops of an aqueous solution (1 in 30) of ferric chloride a white precipitate which becomes brown but not violet. The pure naphthol should give no appreciable ash.

To detect α-naphthol in β-naphthol Jorissen's test (see Table p. 230) may also be used.

For the quantitative estimation of α-naphthol in presence of large proportions of β-naphthol, J. Prochazka and H. N. Herman (*J. Soc. Chem. Ind.*, 1897, **16**, 894) have devised the following process, depending on the greater facility with which α-naphthol combines with diazo-compounds:

27.5 grm. of 90% sodium naphthionate are dissolved in 185 c.c. of water. 6.2 c.c. of sulphuric acid (sp. gr. 1.835) are diluted with 180 c.c. of water and the mixture run slowly into the naphthionate solution, which is continuously stirred to secure a uniform paste. The mixture is cooled to below 5°, and a 10% solution of sodium nitrite, containing 7 grm. of the commercial 98% product, added slowly, stirring constantly. The resulting paste, made up to 750 c.c., is now ready for use.

For the test, 15 grm. of the sample, 200 grm. of a 25% solution of sodium hydroxide solution, and 140 c.c. of a 10% solution of sodium carbonate are heated together until the β-naphthol is dissolved. The solution is cooled to below 5° and made up to 250 c.c. The diazo-compound as prepared is run slowly and carefully into this solution of the sample, which is continually stirred. If the β-naphthol is pure, the resulting azo-compound will precipitate completely in the shape of a fine crystalline powder, and hardly any colour will pass into solution while the first portions of the diazo-compound are being added. On the contrary, if α-naphthol is present, a coloured solution will be formed. As little as 0.1% can be detected. If the rest of the diazo-compound be added, the presence of the α-naphthol

	Naphthalene	α-Naphthol	β-Naphthol
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0.144 grm. of the naphthol is dissolved in 5 c.c. of pure alcohol in a graduated cylinder and 15 c.c. of toluene added. 0.14 grm. of *p*-nitraniline is dissolved in 9 c.c. of dilute hydrochloric acid and diazotised, after thoroughly cooling in a freezing mixture, with 1 c.c. of normal sodium nitrite solution. The diazo solution is poured into the naphthol solution, some water added, and the mixture, shaken and allowed to separate into two layers in a separating funnel. The toluene layer is shaken with 5 c.c. of sodium hydroxide solution and the colour of the liquid compared with that of solutions of β-naphthol made in a similar way from β-naphthol containing known proportions of α-naphthol. These solutions must be freshly prepared, as the colour changes on keeping. This test allows of the estimation of such small quantities of α-naphthol as 0.01 grm.

Detection of β-naphthol in Foods.—The marked antiseptic qualities of β-naphthol render it suitable for use as a food-preservative but it has not been largely employed. For its detection in ordinary foods, the American Association of Official Agricultural

Chemists suggested the following procedure, which covers also the detection of several similar antiseptics (Proc. 14th Ann. Conv., 1897, *A. O. A. C.*, Bull. 51, *U. S. Dept., of Agric.*).

200 grm. of the sample are acidified with dilute sulphuric acid, distilled with open steam, and the first 200 c.c. of the distillate extracted in a separating funnel with about 20 c.c. of chloroform. After being run off, the chloroform is rendered slightly alkaline with potassium hydroxide and heated for a few minutes almost to boiling. Colour changes occur as follows, if an antiseptic of the phenol class is present:

Phenol	Light red, to brown, to yellow, to colourless.
o-Cresol	Lilac with tinge of orange.
β-Naphthol	Deep blue, to green, to brown.
Salol	Light red.

In Bulletin No. 107 (1907) (see also *A. O. A. C.* Methods of Analysis revised Nov. 1, 1919, page 127) the procedure recommended is as follows: extract 200 c.c. of the sample (or of its aqueous extract prepared by macerating 200 to 300 grm. of the sample with water made slightly alkaline with sodium hydroxide and straining through a cotton bag) with 10 c.c. of chloroform in a separating funnel, add a few drops of alcoholic potassium hydroxide to the chloroform extract, and place on a boiling water-bath during 2 minutes. The presence of β-naphthol is indicated by the formation of a deep blue colour which changes through green to yellow.

For the detection of β-naphthol in foods, spices and beverages Y. Kinugasa and H. Tatsuno (*J. Pharm. Soc. Japan*, 1922, No. 479) proceed as follows: the test is a modification of Riegler's method for the detection of nitrous acid in water. To detect β-naphthol in soya sauce, for example, 100 c.c. of the sauce is acidified with 15 c.c of sulphuric acid mixed with an equal volume of water, and shaken with a mixture of equal volumes of ether and petroleum spirit. The extract is evaporated and the residue extracted 3 times with 10 c.c. of petroleum spirit each time, the extracts being evaporated and the residue dissolved in 10 c.c. of water. The solution is filtered and shaken with petroleum spirit (10 c.c.) the extract evaporated, and the residue dissolved in a small quantity of water to which 2 drops of sodium naphionate solution (0.1%), 1 drop of sodium nitrate solution (0.1%) and 1 drop of hydrochloric acid are added. On gradually adding ammonia a rose red colour develops due to the formation of Fast Red A, which dyes red shades on wool and on cotton mordanted with alum. 0.001 mgrm. of β-naphthol in 1 litre responds to the test.

Estimation of β-Naphthol.—This is seldom necessary as the best method of ascertaining the degree of purity of a sample of the commercial article is by means of the m. p. and the qualitative tests already given. The methods that have been suggested for estimating β-naphthol, which will be briefly indicated, are only reliable when applied to the pure substance. Thus, in the picric acid method, α-naphthol, naphthalene, and other hydrocarbons are reported as β-naphthol. If the iodometric method is used, other substances, such as phenols, are generally present which absorb iodine; α-naphthol, for instance, counts as β-naphthol.

1. **Picric Acid Method.**—This is carried out by Küster (*Ber.*, 1894, **27**, 1101) exactly as in estimating naphthalene (pp. 213 and 215) by means of picric acid. A weighed quantity of the substance is digested in a sealed flask (preferably under reduced pressure) on the water-bath, with a measured volume of a saturated aqueous solution of picric acid. The naphthol is converted quantitatively into an insoluble picrate, and the amount of picric acid remaining in solution is ascertained by titration of an aliquot portion with N/10 barium hydroxide (see under *Naphthalene*). As β-naphthol picrate is slightly soluble in water, it is necessary to allow 0.0075 grm. of β-naphthol per 100 c.c. of picric acid solution used, this being the quantity which remains in solution at the ordinary temperature.

2. **Iodometric Method** (Messinger and Vortmann, *Ber.*, 1890, **23**, 2754).—3 grm. of the sample are dissolved in a solution of not less than 3.5 grm. of sodium hydroxide ($= C_{10}H_7OH + 4NaOH$), and the solution diluted to an exact volume, not less than 250 c.c. Ten c.c. of the solution are placed in a small flask, heated to 55°, and N/10 iodine solution added until the liquid shows a yellow colour, indicating excess of iodine. On shaking, a dirty green precipitate may be produced. The liquid is cooled, acidified with sulphuric acid, diluted to 250 c.c., and an aliquot portion titrated with decinormal sodium thiosulphate to ascertain the excess of iodine. The figure for the iodine actually used, calculated to the whole amount taken, and multiplied by 0.3784, will give the amount of β-naphthol present.

J. M. Wilkie (*J. Soc. Chem. Ind.*, 1911, **30**, 398) carefully investigated Messinger and Vortmann's method as applied to phenols.

When a cold aqueous solution of β-naphthol is treated with N/10 iodine an almost quantitative yield of 1-iodo-2-hydroxynaphthalene is obtained, but in presence of a slight excess of alkali hydroxide over that corresponding with the formation of $C_{10}H_7ONa$, a colourless, crystalline product is no longer obtained, but the green amorphous compound of Messinger and Vortmann. In carrying out the quantitative process variable results are obtained according to the excess of iodine used, a result which differs from that obtained with phenol and salicylic acid in which case the absorption of iodine is independent of the alkali and iodine provided that the excess exceeds 60%. The quantitative process is however satisfactory when practised in neutral solution as follows:

2.44 grm. of naphthol are dissolved in 10 c.c. of N/10 sodium hydroxide; if the solution is diluted to 200 c.c. it is N/10 to iodine. 10 c.c. are then transferred to a Jena glass bottle, 150 c.c. of water added at the ordinary temperature and 4 c.c. of N/10 sulphuric acid so as have a feebly alkaline solution. 20 c.c. of N/10 iodine are added and after standing in a bath of water at 55–65°, some sulphuric acid and the residual iodine is titrated with thiosulphate as usual. The action is practically quantitative:

$$C_{10}H_7OH + I_2 = C_{10}H_6I.OH + HI$$

As stated above, Messinger and Vortmann's method is a general method for phenols, and is useless for β-naphthol in presence of such substances as phenol, cresols, salicylic acid, thymol, etc.

β-NAPHTHOL ETHERS

β-Naphthol Methyl Ether (*β-Methoxynaphthalene*) crystallises from light petroleum in small leaflets, m. p. 72°, b. p. 274°. It is used in perfumery under the name *Yara-Yara.*

β-Naphthol Ethyl Ether (*β-Ethoxynaphthalene*), m. p. 37°, b. p. 274–275°, crystallises in large plates from light petroleum. It is used in perfumery under the name *nerolin,* which is also applied to β-methoxynaphthalene.

β-NAPHTHOLSULPHONIC ACIDS

Those sulphonic acids of β-naphthol which are of importance in dyeing will be dealt with in Vol. VI.

Abrastol or asaprol is calcium β-naphtholsulphonate, $(OH.C_{10}H_6SO_3)_2Ca$. For detecting this substance, Bulletin No. 107 (1907) (see also *A. O. A. C.* Methods revised Nov. 1, 1919, p. 128) of the U. S. Dept. of Agriculture, Bureau of Chemistry, gives the following tests.

1. **Sinabaldi's Test.**—Make 50 c.c. of the sample alkaline with a few drops of ammonia and extract with 10 c.c. of amyl alcohol (ethyl alcohol is added if an emulsion is formed). Decant the amyl alcohol, filter if turbid, and evaporate to dryness. Add to the residue 2 c.c. of a mixture of equal parts of conc. nitric acid and water, heat on a water-bath until half the water has evaporated and transfer to a test-tube adding 1 c.c. of water. Then add about 0.2 c.c. of ferrous sulphate solution and an excess of ammonia drop by drop, shaking continuously. If the precipitate is reddish in colour, dissolve it in a few drops of sulphuric acid and add ferrous sulphate and ammonia as before. As soon as a dark coloured or greenish precipitate has been obtained, introduce 5 c.c. of alcohol, dissolve the precipitate in sulphuric acid, shake well and filter. When abrastol is absent this method gives a colourless or light yellow liquid, whilst a red colour is produced when abrastol is present to the extent of 0.01 grm.

2. **Sanglé-Ferrière's Method.**—Boil 200 c.c. of the sample with 8 c.c. of concentrated hydrochloric acid during one hour beneath a reflux apparatus. Abrastol is converted in β-naphthol, which can be detected by the method given on page 229.

Leffmann gives the following test for the presence of abrastol in milk. To 10 c.c. add 0.5 c.c. of mercuric nitrate solution made by dissolving mercury in twice its weight of nitric acid and diluting with 5 vols. of water. If abrastol is present a yellow coloration rapidly appears. In testing wines, acidify with a few drops of dilute sulphuric acid and shake with an equal volume of chloroform or ether. To the chloroform or ethereal layer, a few drops of mercuric nitrate solution are added and the mixture shaken. If abrastol is present the mercury solution turns yellow and finally red. If a fat is examined it should be melted and the abrastol removed by shaking with 20% alcohol. The alcohol is removed by distillation, and the residual aqueous solution is tested with the mercury solution as above.

NITRONAPHTHALENES

The nitronaphthalenes, especially α-nitronaphthalene, are of importance in connection with explosives (see p. 640), as their presence renders nitroglycerin non-sensitive to concussion; when present, even in very small proportion, they prevent dynamite from freezing. They considerably increase the solvent action of nitroglycerin on nitrocellulose.

α-Nitronaphthalene is also of importance as the material from which α-naphthylamine is prepared. It forms pale yellow needles, is easily soluble in alcohol and ether, insoluble in water, m. p. 61°, b. p. 394°. The m. p. is the test of purity of the commercial article.

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Lunge-Keane, *Chemical Technical Methods*, 2nd Ed., Vol. I, p. 315 etseq.
Lunge's *Coal Tar and Ammonia*, 5th Ed., Part II, p. 823 etseq
Reverdin und Fulda, *Tabellarische Uebersicht der Naphthalin Derivate.*

ANTHRACENE, PHENANTHRENE, CARBAZOL, AND OTHER CONSTITUENTS OF THE HIGH BOILING FRACTIONS OF COAL-TAR

BY JOHN H. SACHS, PH. D.

With the synthesis of alizarine from anthracene in 1868–1869 by Caro, Graebe, and Liebermann in Germany, and Perkin in England, the hitherto unimportant high boiling fractions of coal-tar became of great commercial value. During the next 30 years many derivatives of anthracene and anthraquinone were brought into technical importance because of their value as acid and mordant dyes. Early in the twentieth century a new impetus was given to the chemistry of anthracene and anthraquinone by the discovery of Indanthrene, the first of a remarkable series of vat dyes derived from these substances. About a decade later the discovery of Hydron Blue and Ciba Scarlet placed carbazol and acenaphthene in the category of commercially valuable products from the high boiling fractions of coal-tar.

In the distillation of coal-tar, the portion passing over between 270° and 400°, known as anthracene oil, green grease, red oil or green oil, is a heavy greenish or reddish oily liquid whilst hot, and a semi-solid mass when cold. Its boiling range is from 280° to 400° and its sp. gr. is 1.1–1.15. The amount of this fraction obtained depends upon the source of the tar. Clark (*J. Ind. Eng. Chem.*, 1919, 11, 204) states that 23% of coke oven tar boils between 290° and 380°, whilst only 16.2% of gas house tar distils within these limits. He gives the following properties and compositions of the high boiling fractions from these tars:

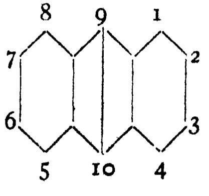
	GAS HOUSE TAR	COKE OVEN TAR
Sp. gr. at 15.5°	1 152	1.143
Phenols, per cent	3.1	1.7
Anthracene, per cent	1.8	1.5
Carbazol, per cent	0.7	0.6
Phenanthrene, etc., per cent	2.6	2.8

The quality of coal used for the production of coke or gas plays an important part also in the quality of the anthracene oil derived from the by-product tar. Scottish or cannel coals produce a tar which yields almost valueless high boiling fractions because of the presence of troublesome paraffins which are removed only with great difficulty in the working up of these fractions.

Anthracene oil, according to Lunge (Lunge, *Coal Tar and Ammonia*, Vol. II, Ch. 7), contains essentially the following compounds: Naphthalene, Methylnaphthalene, Anthracene, Phenanthrene, Acenaphthene, Diphenyl, Methylanthracene, Pyrene, Chrysene, Retene, Fluorene, Fluoranthrene, Chrysogene, Benzerythrene, Carbazol, Acridine, and Hydroacridine; but along with these substances there is a mixture of high boiling oils of which very little is as yet known.

Many patents have been granted on various processes for the separation of the various constituents of anthracene oil. At the present time it may be said that the method generally followed consists in a cold hydraulic pressing of the oil, or filtration on a centrifuge, followed by a repetition of the same operation at a somewhat higher temperature, 40–50°. By this treatment there results a sandy, oily, granular mass which may contain 30–40% anthracene, 15–20% of carbazol, and 40–50% of phenanthrene and other compounds. The separation of the compounds from each other may be brought about in many ways, namely; by fractional crystallisation from various solvents such as pyridine, solvent naphtha, petroleum spirit, liquid sulphur dioxide, and liquid ammonia, or by taking advantage of the fact that carbazol combines with potassium hydroxide with the elimination of water at high temperatures and the sublimation or separation by solvents of the unchanged anthracene, phenanthrene, etc.

Anthracene
$C_{14}H_{10}$



m. p. 213°. b. p. 351°
Picrate, Red, m. p. 138°

Anthracene, the most important constituent of the high boiling fractions of coal-tar, can be prepared synthetically by numerous methods, none of which, however, have as yet been used on a commercial scale. Therefore, the sole source of the commercial article is coal-tar. Until recently Germany and England led in the production of anthracene, but in line with the rapid growth of the American dye industry since the great war, a considerable production has been reached in this country.

When very pure, anthracene crystallises in colourless rhomboidal plates or scales, which exhibit a beautiful blue fluorescence. Although it melts at 213°, it sublimes even at 120° in micaceous scales. Chemically, it is a very stable body, distilling almost unchanged in admixture with potassium hydroxide.

Anthracene is insoluble in water, and in dilute acid and alkaline solutions. It is sparingly soluble in hot or cold alcohol and ether, but readily so in hot benzene, toluene, pyridine, and solvent (coal-tar) naphtha. (See page 256.)

If picric acid be added to a solution of anthracene in boiling benzene, a compound having the formula $C_{14}H_{10}.C_6H_2(NO_2)_3OH$ is formed. On cooling, the picrate separates in ruby red needles which melt, when pure, at 138° and are soluble with red colour in small proportions of alcohol, but on adding more alcohol or water the compound dissociates and the liquid is decolorised.

When acted upon by various strengths of nitric acid at various temperatures, anthracene is converted into mixtures of anthraquinone and nitroanthraquinones. When a mixture of nitric acid and glacial acetic acid is allowed to act at 15–20° upon anthracene dissolved in glacial acetic acid, there results 9-nitroanthracene, m. p. 145–146°, and 9, 10-dinitroanthracene, m. p 294°. The oxidation of anthracene to anthraquinone by means of nitric acid has been studied very extensively and a number of patents covering the various processes developed have been granted.

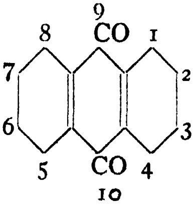
On gentle heating, concentrated sulphuric acid dissolves anthracene with greenish colour and at a higher temperature forms anthracene 2-mono sulphonic acid, 2.6- and 2.7-disulphonic acids. The sulphonation with fuming sulphuric acid is violent even at comparatively low temperatures.

By the action of bromine or chlorine, anthracene is converted into various bromo and chloro derivatives, the 9 and 10 positions being the most readily attacked. When treated with dry chlorine it readily yields 9.10-dichloranthracene, a lemon yellow crystalline substance resembling picric acid. One of the commercial methods for the manufacture of artificial alizarine depends upon this reaction.

By exposing anthracene suspended in benzene or xylene to the action of direct sunlight or ultra-violet rays, there separates a dimolecular modification found by Orndorff and Cameron (*Am. Chem. Jour.*, 1895, 658) to have the formula $(C_{14}H_{10})_2$ and called by them dianthracene. It melts at 270–280° with dissociation to anthracene, is not soluble in benzene, is not attacked by bromine or nitric acid, and does not combine with picric acid. It is converted into anthraquinone with chromic acid or warm fuming nitric acid. A process for the separation of anthracene from carbazol, phenanthrene, etc., based upon this behavior of anthracene, has recently been patented.

By the reduction of anthracene with sodium amalgam and alcohol, anthracene dihydride, $C_{14}H_{12}$, m. p. 108°, is formed. This compound can also be prepared by the condensation of methylene bromide and benzene by means of aluminium chloride. The two hydrogen atoms are therefore in the 9–10 positions. Through reduction of anthracene by means of hydriodic acid, or hydrogen and nickle at 200–250°, there results anthracene tetra-, hexa-, octo-, and perhydride, which compounds melt respectively at 89°, 63°, 71°, and 88°. The di- and tetra-hydrides are said to occur in anthracene oil.

Anthraquinone $C_{14}H_8O_2$



m. p. 285°

b. p. 382°

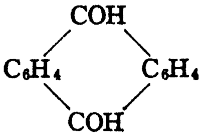
Anthracene can be converted into anthraquinone by means of various oxidising agents, chromic acid being the best and most common. When nitric acid is used for the reaction the formation of nitro-anthraquinones is prevented only with difficulty.

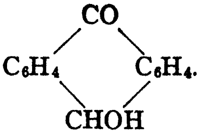
As usually prepared, anthraquinone appears as a felted mass of delicate crystalline needles or plates of a yellowish or pale buff colour. When purified by sublimation it is obtained in long lemon yellow needles or golden yellow prisms.

Anthraquinone is neutral in reaction, and is insoluble in water and in dilute acid and alkaline solutions. It is sparingly soluble in alcohol and ether, more so in benzene and toluene, and readily in hot nitrobenzene, phenol, and cresol. It is very stable, resisting the action of many reagents. It is not affected by hot hydrochloric acid, or by boiling with solutions of sodium or potassium hydroxide. It dissolves in hot concentrated nitric acid and is deposited in crystals on cooling, a more complete separation occurring when the acid is poured into water.

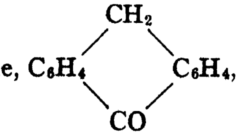
Anthraquinone dissolves unchanged in concentrated sulphuric acid, and the solution may be heated to 100° without action of the acid upon the anthraquinone. On exposing moderately concentrated solutions to a moist atmosphere, the anthraquinone is gradually redeposited in long needle-like crystals or flat prisms, or it may be obtained in a more finely divided amorphous state by pouring the acid solution slowly into boiling water. Due to the fact that the impurities usually occurring in crude anthraquinone are acted upon by hot concentrated sulphuric acid with the formation of their soluble sulphonic acids, whilst anthraquinone is unchanged, treatment with sulphuric acid is employed for the purification of crude anthraquinone. When strongly heated with concentrated sulphuric acid, or at a more moderate temperature with fuming acid, anthraquinone is converted in whole or in part into a mixture of anthraquinone 2-mono sulphonic acid, 2.6- and 2.7- disulphonic acids. In the presence of a small quantity of mercury or its salts the sulphonation leads to the formation of anthraquinone 1-monosulphonic acid, 1.5- and 1.8- disulphonic acids. All of these sulphonic acids have become of great commercial importance in late years, being the parent substance of a large number of valuable dyes. The various sulphonic acids may be obtained by nearly neutralising the greatly diluted sulphonation mass with sodium hydroxide and fractionally crystallising the sodium salts of the acids. Anthraquinone-2-mono sodium sulphonate, the so-called "Silver Salt" of commerce, and the most important of these salts, crystallises in brilliant pearly scales. When fused with potassium hydroxide, with or without the presence of an oxidising agent, it is converted into alizarine.

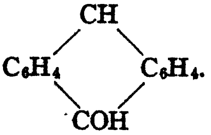
When fused with potassium hydroxide at 250° anthraquinone is converted into potassium benzoate; when distilled from soda-lime, benzene and diphenyl are formed, and when heated with potash-lime, the principal product of the reaction is diphenyleneketone.

By the action of reducing agents anthraquinone is converted into various compounds, depending, as in the case of the reduction of nitrobenzene, upon whether the reduction is brought about in acid or alkaline solution. When zinc powder and sodium hydroxide are used as the reducing agent the product of the reaction is anthrahydroquinone. 

which also exists in another form, oxanthron, 

Anthrahyroquinone dissolves in warm dilute sodium hydroxide solution, with a splendid red colour, and this property furnishes a very simple and at the same time a reliable qualitative test for anthraquinone. If a small sample of anthraquinone is shaken with the exclusion of air in a warm, dilute solution of sodium hydroxide containing a little zinc dust, or better, a small amount of sodium hydrosulphite, $Na_2S_2O_4$, the characteristic red colour of a solution of the sodium salt of anthrahydroquinone will appear. By blowing air through the solution the red colour will disappear owing to the oxidation of the anthrahydroquinone into anthraquinone.

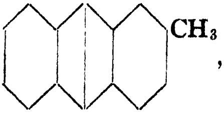
When anthraquinone is reduced in sulphuric or acetic acid solution by means of tin or aluminium the product of the reaction is the relatively stable anthrone, 

which also exists in another form, anthranol, 

The former substance can be converted into the latter by boiling with aqueous sodium hydroxide, anthranol being soluble in this medium with a clear straw yellow colour.

With hydriodic acid at 150°, or with zinc dust and aqueous ammonia, anthraquinone is reduced to anthracene.

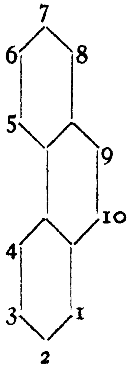
Methyl-Anthracene $C_{15}H_{12}$,



, m. p. 207°. b. p. above 360°.

This substance occurs in small quantities in coal-tar and is very similar in its properties to anthracene. It can be prepared by reduction of chrysophanic acid, a hydroxylated derivative of methyl-anthraquinone. Methyl-anthracene crystallises from hot alcohol, in which it is sparingly soluble in thin pale yellow plates, and when sublimed it shows a greenish fluorescence. On oxidation it is converted into methyl-anthraquinone, m. p. 176–177°, and finally into anthraquinone-2-carboxylic acid. By the action of sunlight it is polymerised into dimethyldianthracene, m. p. 229°.

Phenanthrene
$C_{14}H_{10}$



m. p. 100° b. p. 340°
Picrate, Yellow m. p. 144°

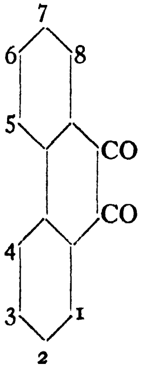
Phenanthrene occurs in considerable quantities in crude anthracene, and may be separated from other constituents of this mixture by extraction with cold benzene, toluene, or solvent naphtha, in which solvents it is readily soluble. It can be purified by crystallisation from alcohol, from which solvent it crystallises when pure in colourless lustrous plates. The melting point of phenanthrene is much lower than that of anthracene, but it sublimes less readily than the latter, although its boiling point is lower. It is distinguished from anthracene by its behavior with picric acid, antimony and bismuth chlorides, and chromic acid.

When treated with chlorine, phenanthrene yields various substitution products, the first one formed being 9.10 dichlorphenanthrene, m. p. 161°. Further chlorination leads to 2.9.10-trichlorphenanthrene, m. p. 124°, and by prolonged chlorination octochlorphenanthrene, m. p. 270–280°, results. The addition of bromine to a suspension of phenanthrene in carbon bisulphide first leads to a simple addition of halogen with the formation of phenanthrenedibromide, which compound loses one molecule of HBr and passes into 9-bromphenanthrene, m. p. 63°. Further bromination leads to the formation of 4.9 (4.10) dibromphenanthrene m. p. 112–113°.

When nitrated in acetic anhydride with a mixture of nitric acid and acetic anhydride, phenanthrene is converted into 9 (10)-nitrophenanthrene, m. p. 116–117°. When treated with methyl alcoholic potassium hydroxide this compound passes into phenanthraquinonemonoxime.

Phenanthrene when treated with concentrated sulphuric acid at 100° is readily sulphonated, the products being a mixture of 2, 3, and 9- phenanthrene sulphonic acids. The corresponding sulphonchlorides melt respectively at 156°, 108°, and 125°.

Phenanthraquinone



$C_{14}H_8O_2$ m. p. 198°

Just as anthracene when treated with a mixture of chromic anhydride and acetic acid is oxidised to anthraquinone, so phenanthrene, when similarly treated, passes into phenanthraquinone. However, the properties of the two compounds are entirely different. Anthraquinone is very stable to oxidising agents, whereas phenanthraquinone is readily oxidised to diphenic acid, which in turn can be further oxidised to phthalic acid. The constitution of phenanthrene follows from these reactions. Anthraquinone is practically insoluble in water and but sparingly soluble in warm alcohol, ether and benzene. Phenanthraquinone is slightly soluble in water and dissolves freely in warm alcohol, ether, and benzene, from which solvents it crystallises in dark red needles. Ignited with soda-lime phenanthraquinone produces diphenyl in very good yields, whilst anthraquinone, when similarly treated, is converted into benzene. Anthraquinone does not form an addition product with the acid sulphites of the alkali metals, whilst phenanthraquinone, when warmed with a solution of these substances, readily passes into solution, from which phenanthraquinone can be separated by the addition of hydrochloric acid. This reaction may be used for the detection of phenanthrene in anthracene. The hydrocarbon or mixture of hydrocarbons under examination is oxidised in glacial acetic acid with chromic anhydride and the reaction mixture is diluted with water and filtered. The oxidation product is washed first with a dilute solution of sodium hydroxide and then extracted with a solution of sodium acid sulphite. A precipitate resulting on the addition of acid to the filtered solution indicates the presence of phenanthraquinone or pyrenequinone.

If a few drops of commercial toluene or benzene be added to a dilute solution of phenanthraquinone in glacial acetic acid, the solution thoroughly cooled, commercial sulphuric acid added drop by drop, and the resulting solution treated with water, after a few minutes, a colouring matter separates out which is dissolved with a splendid reddish blue colour on agitation with ether. This reaction depends upon the presence of thiophene or methyl-thiophene in the benzene or toluene respectively.

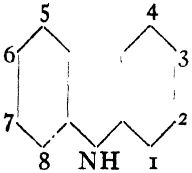
A large number of halogen derivatives of phenanthraquinone have been prepared, but they are of relatively little importance. The same may be said of its nitro- and sulphonic acid derivatives.

Pseudophenanthrene = $C_{16}H_{12}$ m. p. 115°

Picrate, Light Red Needles, m. p. 147°.

This substance occurs in small quantities in that portion of crude anthracene which is soluble in ethyl acetate. It forms large white, glistening plates, exhibiting no fluorescence. It is distinguished from phenanthrene by the fact that its picrate separates on mixing cold saturated alcoholic solutions of the hydrocarbon and picric acid. On oxidation with chromic acid it is converted into a yellow quinone having a melting point of 170° and a ready solubility in alcohol and cold benzene.

Carbazol. Dibenzpyrrol. Diphenyleneimide



$C_{12}H_9N$

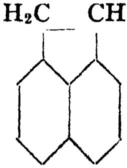
m. p. 238°. b. p. 351°.
Picrate. m. p. 182°.

Carbazol usually occurs in crude anthracene to the extent of 10 to 20%. Although it is usually considered as a weak acid, it exhibits, like pyrrol, the properties of a very weak base, forming with picric acid a stable picrate. When melted with potassium hydroxide, or better, with potash mixed with a little lime, it readily forms the potassium salt, with the elimination of water. The best method for the separation of carbazol from the other constituents of crude anthracene depends upon this reaction, and consists in the fusion of the anthracene with sufficient potash to combine with the carbazol, and the separation of the other constituents by distillation in vacuum, by extraction with solvents, or by the separation of the two layers which form when the fused mass is allowed to stand quietly in the melted state. The potassium carbazolate is readily hydrolysed by boiling with water, and the carbazol can be further purified by sublimation or by crystallisation from toluene. When pure, it crystallises in colourless, fluorescent scales or plates which resemble anthracene. It is insoluble in water. It dissolves readily in hot alcohol, ether, chloroform, benzene, or toluene, and crystallises when the warm solutions are allowed to cool.

When potassium carbazolate is heated with methyl or ethyl bromide the corresponding methyl or ethyl carbazol is formed, melting points 87° and 68° respectively. The latter compound is now of technical importance, being the primary intermediate necessary for the manufacture of Hydron Blue G. Carbazol itself is used for the manufacture of Hydron Blue R.

With nitric acid, carbazol yields N-nitrosocarbazol, which, when treated with mineral acids passes into 3-nitrosocarbazol. In pure cold sulphuric acid it dissolves, when pure, with a yellow colour, but in the presence of minute traces of nitric or chromic acid, chlorine or other oxidising agents, an intense green coloration is produced. A method for the colorimetric estimation of nitrates in water depends upon the reaction. When fused with oxalic acid carbazol passes into tricarbazolcarbinol or Carbazol Blue.

Acenaphthene. Periethylenenaphthalene.



m. p. 95° b. p. 277°

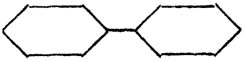
Picrate—Orange Yellow Needles
m. p. 161–162°.

Acenaphthene occurs chiefly in that fraction of coal-tar boiling between 270° and 300°, and crystallises from the 280° to 290° fraction on cooling. It may be purified by crystallisation from hot alcohol or coal-tar naphtha, followed by careful sublimation. From alcohol it crystallises in long, colourless, lustrous needles, and from heavy coal-tar naphtha in hard, brittle crystals.

On oxidation with chromic acid, acenaphthene is first converted into acenaphthenquinone, melting point 261°. This compound is now of technical importance, being a component of Ciba Scarlet, a valuable vat dye. Further oxidation leads to the formation of naphthalic acid, or naphthalene-1.8-dicarboxylic acid. The compound when heated to 180° passes, without melting, into naphthalic acid anhydride, melting point 266°.

Acenaphthene has an odour similar to that of naphthalene, is readily acted upon by bromine, sulphonates readily, and yields a nitro compound when treated with nitric acid.

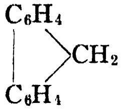
Diphenyl, Phenylbenzene, Biphenyl $C_{12}H_{10}$



m. p. 71°. b. p. 254°.

Diphenyl is found in small quantities in that fraction of coal-tar boiling between 240 and 300°. It can be prepared synthetically by numerous methods, the best results being obtained by the action of metallic sodium upon brombenzene, or of copper powder upon iodobenzene. It may be isolated from the above fraction of coal-tar by sulphonation, whereby the methyl- and dimethyl-naphthalene present are converted into water soluble sulphonic acids. On cooling the unsulphonated fraction to −15° the diphenyl separates out. It dissolves readily in alcohol and ether, and crystallises from these solvents in large, colourless scales.

Fluorene $C_{13}H_{10}$, Diphenylenemethane, m. p. 113°, b. p. 295°.

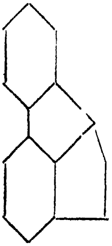


$$\begin{array}{l} C_6H_4 \\ \mid \quad \rangle CH_2 \\ C_6H_4 \end{array}$$

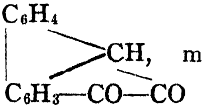
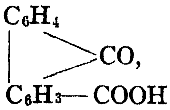
Picrate, m. p. 81°.

Fluorene is found in that fraction of coal-tar boiling between 270° and 300°. It can best be separated from the other constituents of this fraction by the action of sodium amide, whereby it is converted into a sodium salt, $(C_6H_4)_2$: CHNa, from which the other bodies may be removed by extraction or distillation Fluorene is readily soluble in hot alcohol, ether, benzene and carbon disulphide, and crystallises from these solvents in colourless scales which show a violet fluorescence. When brominated in boiling chloroform it forms dibromfluorene, m. p. 164°, and when nitrated in glacial acetic acid it is converted into nitrofluorene, m. p. 153°. By reduction with hydriodic acid and phosphorus, or by hydrogen and nickel it is converted into perhydrofluorene, b. p. 256°–258°. It is interesting to note that a hexahydro derivative of fluorene occurs as such in coal-tar and can be obtained therefrom by extraction with benzene, or by distillation *in vacuo Ber.*, 1911, **44**, 2486). By the action of chromic acid, fluorene is oxidised to fluorenone, diphenyleneketone, $(C_6H_4)_2CO$, m. p. 84°, b. p. 34°.

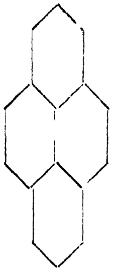
Fluoranthrene, Idryl, $C_{15}H_{10}$, m. p. 110°, b. p. 250°.



Picrate, Orange Needles, m. p. 182°

Fluoranthrene occurs in the highest boiling fractions of coal-tar and is best separated from the accompanying pyrene by the fractional crystallisation of its picrate from alcohol. Fluoranthrene crystallises from dilute alcohol in large shining plates and from strong alcohol in needles. It dissolves in warm concentrated sulphuric acid with a greenish blue colour, changing at a higher temperature to blue and at length turning brown. It is converted by the action of chromic acid into fluoranthrenequinone,  $\begin{array}{l} C_6H_4 \\ \mid \quad > CH, \\ C_6H_3-CO-CO \end{array}$ m.p. 188°, which substance can be still further oxidised with the elimination of carbon dioxide to diphenyleneketone-carboxylic acid,  $\begin{array}{l} C_6H_4 \\ \mid \quad > CO, \\ C_6H_3-COOH \end{array}$ a derivative of fluorene.

Pyrene, $C_{16}H_{10}$, m. p. 149°, b. p.$_{60}$ 250°.



Picrate, Red Needles, m. p. 222°.

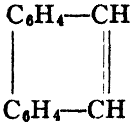
Pyrene, together with fluoranthrene, occurs in the highest boiling fractions of coal-tar. On extracting these with carbon disulphide, evaporating the filtered solution to dryness, dissolving the residue in hot alcohol, and adding an alcoholic solution of picric acid, the picrate separates on cooling and can be purified by fractional crystallisation from alcohol. The hydrocarbon, which may be obtained by treating the picrate with ammonia, crystallises from alcohol in colourless plates.

On oxidation with chromic acid and acetic acid, pyrene passes successively to pyrenequinone, $C_{16}H_8O_2$ and to pyrenic acid, $C_{12}H_6$-$CO(COOH)_2$, a keto-dicarboxylic acid which lends itself readily to anhydrid and imide formation, and which on distillation yields pyrene-ketone $C_{12}H_8CO$, m. p. 141°.

Chrysene $C_{18}H_{12}$, m. p. 250°, b. p. 448°.

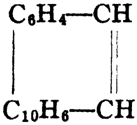
Picene $C_{22}H_{14}$, m. p. 264°, b. p. 518–520°.

These two substances bear the following relation to phenanthrene, to which they are structurally closely allied. Picene, however, does not occur in commercial crude anthracene, but is found in the residue left upon the distillation of petroleum.



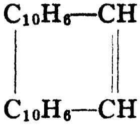
$$\begin{array}{ccc} C_6H_4 & - & CH \\ | & & \| \\ C_6H_4 & - & CH \end{array}$$

Phenanthrene



$$\begin{array}{ccc} C_6H_4 & - & CH \\ | & & \| \\ C_{10}H_6 & - & CH \end{array}$$

Chrysene



$$\begin{array}{ccc} C_{10}H_6 & - & CH \\ | & & \| \\ C_{10}H_6 & - & CH \end{array}$$

Picene

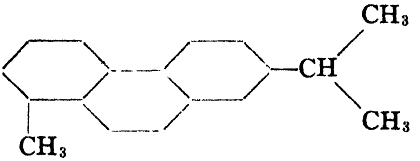
Chrysene is extracted from the highest boiling fraction of coal-tar, which consists chiefly of this hydrocarbon and pyrene. By repeated extractions of this fraction with carbon disulphide all hydrocarbons, excepting chrysene, are removed, and the resulting compound can then be obtained in a comparatively pure state by crystallisation from petroleum naptha (b. p. 140–160°), from which it separates in golden yellow scales. The yellow colour of the hydrocarbon is due to the presence of small amounts of chrysogene, of which little is known.

Chrysene crystallises in plates, or when quite pure, in colourless rhombic scales, with a deep reddish violet fluorescence. On adding a small amount of the hydrocarbon to a solution of formaldehyde in sulphuric acid, a reddish violet colour is produced which is discharged on the addition of water. With picric acid in benzene solution, chrysene forms a picrate which crystallises from this solvent in red needles, which are decomposed by alcohol. By treating anthracene and chrysene together in a boiling alcoholic solution with nitric acid, a well-defined molecular compound of dinitroanthraquinone and chrysene separates out on cooling. By reduction of the complex with tin and hydrochloric acid the dinitroanthraquinone is converted into the diamine and the chrysene remains unchanged. A method for the separation of chrysene from other hydrocarbons is based upon this reaction (*J. pr. Chem.* (2) **9**, 250–270).

Chrysene lends itself readily to sulphonation and nitration, forming a sulphonic acid when heated with concentrated sulphuric acid, and a mono-, di-, and tetra-nitro derivative, depending upon the extent of nitration, with nitric acid. On oxidation with chromic acid, chrysene passes into **chrysoquinone**, $C_{18}H_{10}O_2$, m. p. 235°, which is characterised by yielding a blue solution with sulphuric acid.

Picene, a constituent of the residues left upon the distillation of petroleum, also occurs in lignite tar. It is very slightly soluble in most organic solvents, the best being crude cymol. Concentrated and fuming sulphuric acids dissolve it, forming an emerald green solution, and with the former solvent the colour passes successively to blue, bluish-grey, and grey when the solution is heated. When strongly heated with sulphuric acid, picene yields sulphonic acids which are characterised by the blue-green fluorescence of their aqueous solutions. With picric acid, picene forms a red crystalline compound, easily dissociated by water and alcohol. It is an orange-red crystalline powder, which, on heating, is partly decomposed and partly sublimed in the form of thin needles which melt at 190°. By the bromination of picene in chloroform, dibrompicene, m. p. 294–296°, is formed.

Retene, 1-methyl-7-isopropylphenanthrene.



m. p. 98°, b. p. 394°.

Picrate, m. p. 123°.

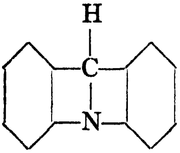
Retene is found chiefly in the tar from many conifers and in a number of asphalts, from the highest boiling fractions of which it can be separated. By oxidation with chromic acid it is converted into 1-methyl-7-isopropylphenanthraquinone, m. p. 197°. It reacts with sulphur, yielding a compound having a m. p. of 86°, and on being reduced with hydrogen in the presence of nickel it yields retenedodecahydride.

Chrysogene is the compound which imparts to impure chrysene its yellow colour. Its formula has not been established, although it is known to contain over 94% of carbon. It is isolated from crude chrysene by frequent crystallisations from coal-tar naphtha, and washing with ether and alcohol. It crystallises from alcohol in yellow, cohering scales, which if very thin are pink, with a gold green reflection. It is but slightly soluble in most organic solvents, dissolving in 2,500 parts of cold, or in 500 parts of boiling benzene, and in 10,000 parts of cold, or 2,000 parts of boiling glacial acetic acid. In sunlight its solutions become rapidly bleached, and yield a colourless crystalline compound, which, on fusion becomes orange yellow. The presence of 1/1000 part of chrysogene imparts an intense yellow colour to naphthalene and other hydrocarbons. It melts at 280–290° with partial decomposition, and dissolves without visible change in concentrated sulphuric acid.

Benzerythrene—Triphenylbenzene, $C_{24}H_{18}$, $C_6H_3(C_6H_5)_3$.

This hydrocarbon forms the very last product obtained in the distillation of coal-tar pitch, and may thus be separated without difficulty. After nearly all the other substances have passed over, the benzerythrene appears as a vapour which can readily be condensed to a bright red powder. This product, however, contains much chrysene and other substances which can be separated only with difficulty. When pure, benzerythrene forms white, shining scales, which melt at 307–308°, and are but slightly soluble in alcohol, or even in boiling glacial acetic acid, but are more soluble in hot benzene. In concentrated sulphuric acid benzerythrene dissolves with a green colour. The symmetrical form, *i. e.*, 1, 3, 5-triphenylbenzene, which melts at 169°, can be synthesised by heating acetophenone with phosphorus pentoxide.

Acridine $C_{13}H_9N$ m. p. 110°, b. p. above 360°.

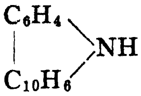


Picrate—Canary Yellow

m. p. 208°.

Crude anthracene contains a number of basic substances, among them being acridine, which can be separated by extraction with dilute sulphuric acid and addition of sodium dichromate to the acid solution, whereby the acridine chromate crystallises out. The salt may be purified by recrystallisation from water and then decomposed with ammonia. The base can then be purified by recrystallisation from hot water. It crystallises in small colourless needles, or four-sided rhombic prisms, which sublime even at 100°. It is sparingly soluble in hot water, but readily soluble in alcohol, ether or carbon disulphide, the solutions showing a blue fluorescence. When inhaled either as a dust or vapour it causes violent sneezing, and in solution both it and its salts cause troublesome irritation to the skin. Acridine exhibits a feeble alkaline reaction, and combines with acids to form a series of yellow salts, all of which are readily crystallisable, and most of them easily soluble. On account of the weakness of the base these salts decompose on boiling with large quantities of water. When nitrated acridine yields tri-nitro compounds melting at 154° and 214° respectively. When oxidised with potassium permanganate it passes into 2.3-quinolinedicarboxylic acid. When reduced with zinc and hydrochloric acid, acridine yields dihydroacridine, $NH(C_6H_4)_2CH_2$, m. p. 168°, a compound which reduces ammoniacal silver solution. Dihydroacridine occurs as such in coal-tar.

Phenylnaphthylcarbazol. m. p. 330°



$$\begin{matrix} C_6H_4\diagdown & \\ | & >NH \\ C_{10}H_6\diagup & \end{matrix}$$

This substance is obtained by subliming the residue remaining after distilling crude anthracene. It has been prepared synthetically by passing phenyl-β-naphthylamine through a hot tube (*Ber.*, 1879, **12**, 2242). When obtained from coal-tar it is coloured intensely yellow, but only by the presence of some unknown impurity; for, on being fused with potassium hydroxide, it turns white. It is practically insoluble in cold alcohol, benzene, toluene or glacial acetic acid, and but sparingly soluble in hot toluene or absolute alcohol. The solutions in these solvents are characterised by an intense greenish blue fluorescence. In its reactions, it is very similar to carbazol. On oxidation with chromic acid it yields a quinone of the formula $C_{16}H_4N_2O_2$, which forms reddish needles and resists further oxidation.

Paraffins. C_nH_{2n+2}.

In the crude anthracenes produced from cannel or Scotch coals, a solid paraffin is likely to be present in considerable quantity, and is a highly objectional impurity, because of the great difficulty in obtaining pure anthraquinone from such an anthracene. These paraffins, according to Perkin, are unlike ordinary paraffin, melting at a higher temperature and being but slightly soluble in petroleum spirits and naphtha.

Solubilities of the Various Constituents of the High Boiling Constituents of Coal-tar:

Owing to the fact that the majority of the compounds occurring in the high boiling fractions of coal-tar are of little importance, little is known concerning their properties. According to Bechi (*Ber.*, 1879, **12**, 1978) the solubilities of several of the more important of these substances, together with that of anthraquinone, in toluene and absolute alcohol, are as follows:

	100 parts toluene dissolve		100 parts absolute alcohol dissolve	
	Cold	100°	Cold	Boiling
Anthracene	0.92 at 16.5°	12.94	0.076 at 16°	0.83
Phenanthrene	33.02 at 16.5°	In all proportions	2.62 at 16°	10.08
Carbazol	0.55 at 16.5°	5.46	0.92 at 14°	3.88
Chrysene	0.24 at 18.0°	5.39	0.097 at 16°	0.17
Pyrene	16.54 at 18.0°	Very soluble	1.37 at 16°	3.08
Phenylnaphthylcarbazol	Scarcely soluble	0.39–0.57	Scarcely soluble	0.25
Anthraquinone	0.19 at 15.0°	2.56	0.05 at 18°	2.249

More recently the solubilities of anthracene, phenanthrene, and carbazol in a large number of solvents have been determined by Clark (*J. Ind. Eng. Chem.*, 1919, II, 204). His results are as follows:

PARTS OF ANTHRACENE, CARBAZOL, AND PHENANTHRENE SOLUBLE IN 100 PARTS OF SOLVENTS

Solvent	At 15.5° C.			At 30° C.			At 50° C.			At 80° C.			At 100° C.		
	Anth.	Carb.	Phen.	Anth.	Carb.	Phen.	Anth.	Carb.	Phen.	Anth.	Carb.	Phen.	Anth.	Carb.	Phen.
Benzene	1.04	0.72	16.72	2.10	1.01	40.10	.....	5.05	.....	.	.....	.....	.....	.....	Above the melting point of phenanthrene
Toluene	0.53	0.42	13.80	1.90	0.78	29.10	3.10	1.60	.....	7.88	2.90	.....	12.20	4.78	
C. P. solvent naphtha refined	0.46	0.48	12.52	1.42	0.70	22.42	2.90	1.37	30.8	6.58	3.00	84.4	10.10	3.72	
Crude coal-tar solvent naphtha	0.50	0.54	15.30	1.71	0.94	31.80	3.25	1.70	74.2	7.20	3.84	243.0	8.82	7.00	
Heavy coal-tar naphtha	0.32	0.48	11.94	1.35	0.75	21.30	3.10	1.52	60.3	7.65	3.63	193.0	10.53	4.70	
Chloroform	0.83	.....	18.70	1.64	0.60	29.20	7.10	1.08	.....	.....	.....	.....	.....	.....	
Carbon disulphide	0.52	.....	26.42	1.62	0.44	.....	.....	.....	.....	.....	.....	.....	.....	.....	
Acetone	0.55	6.12	15.08	1.42	9.74	22.40	2.48	62.30	.....	.....	.....	.....	.....	.....	
Light pyridine	0.85	12.45	25.54	2.15	16.90	38.00	4.10	26.74	78.9	11.22	66.80	241.0	16.72	.....	
Heavy pyridine	0.38	2.72	20.00	1.40	4.10	24.50	2.98	10.57	64.7	7.87	16.34	182.0	8.82	22.87	
Hydrated pyridine	Nil	0.42	0.43	Nil	0.81	1.32	0.001	1.90	7.4	1.53	4.70	11.1	.....	.....	
Carbon tetrachloride	0.67	0.09	7.40	1.15	0.11	11.24	1.30	0.30	.....	.....	.....	.....	.....	.....	
Gasoline	0.12	0.11	4.53	0.37	0.12	6.30	0.76	0.16	.....	.....	.....	.....	.....	.....	
Ether	0.70	2.54	8.93	1.03	2.90	15.24	.....	.....	.....	.....	.....	.....	.....	.....	

Compounds of Solid Hydrocarbons with Picric Acid.—Most of the constituents of crude anthracene form characteristic crystalline compounds with picric acid; which have the general formula $MC_6H_2(NO_2)_3OH$, in which "M" represents a molecule of the hydrocarbon. In some instances this property affords a valuable means of identifying the hydrocarbon. These so-called "picrates" can best be prepared by mixing a hot benzene solution of the hydrocarbon under examination with a hot benzene solution of the requisite amount of picric acid, and allowing the mixture to cool, whereby the addition compound separates out. In some cases hot alcohol may be substituted for the benzene. These substances are relatively unstable, undergoing dissociation when treated with water or ammonia, and in some cases even with alcohol. The following is a description of the compounds of picric acid with the more important substances of this class.

Naphthalene is the only solid hydrocarbon, except pyrene and pseudophenanthrene, giving a precipitate when its cold alcoholic solution is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of yellow needles, melting at 149°.

Diphenyl forms no definite crystalline compound.

Acenaphthene.—The compound forms orange-yellow needles on cooling the boiling alcoholic solution, m. p. 161–162.

Fluorene.—The compound crystallises from benzene in slender red needles, melting at 81°.

Phenanthrene.—The compound crystallises from benzene in yellow needles, melting at 144° and soluble in hot alcohol without decomposition.

Pseudophenanthrene.—The compound forms readily on mixing saturated cold alcoholic solutions of the hydrocarbon and picric acid. It crystallises in light-red needles, melting at 147°.

Anthracene.—The compound is deposited from solution in hot benzene in ruby-red crystals, very soluble, with red colour, in a little alcohol, the solution being decolorised and the compound decomposed on adding more alcohol, m. p. 138°.

Fluoranthrene.—The compound forms reddish-yellow needles, melting at 182°, difficultly soluble in cold alcohol, and decomposed by boiling with water.

Pyrene.—The compound is deposited from hot alcohol as a red crystalline precipitate or long dark red needles, melting at 222°, nearly insoluble in cold alcohol, but very soluble in benzene and decomposed slowly by boiling with water.

Retene.—The compound forms orange-yellow needles, readily soluble in alcohol, m. p. 123°.

Chrysene.—The compound crystallises from benzene in orange needles. It is decomposed by cold alcohol.

Benzerythrene.—The compound is deposited from very concentrated, hot alcoholic solutions in brownish-yellow flocks.

Carbazol.—The compound forms large red prisms, melting at 182°.

Acridine forms a true picrate which is a canary-yellow crystalline salt, which is also wholly insoluble in cold, and is partially decomposed by boiling water. It melts at 208°, and is but slightly dissolved by alcohol or benzene, even when boiling.

The reaction with picric acid has been made the basis of a method of estimating several of these hydrocarbons and their derivatives (*Ber.*, 1894, **27**, 1101).

If substances that form insoluble compounds with picric acid be digested on the water-bath with a measured quantity of an aqueous solution of picric acid, nearly saturated at ordinary temperatures—about N/20—the original substance gradually disappears, and in its place an equivalent quantity of the picric acid compound separates quantitatively, either at once or on cooling. The amount of picric acid in the original solution and in an aliquot portion of the filtrate from the molecular compound can be estimated by titration with barium hydroxide (using lacmoid as indicator), and the quantity of picric acid contained in the precipitate calculated.

The digestion on the water-bath must take place in hermetically closed vessels. The substance to be determined, together with the measured volume of picric acid of known strength in excess, is placed in a flask, which must be nearly filled with the solution. The flask is closed with a good india-rubber stopper, through which passes a tube about 7 cm. long. The tube is sealed at the lower end, and about 1.5 cm. above the sealed end a small hole is blown in the side. When the side hole is just below the stopper, the air in the flask may be pumped out; then, on withdrawing the tube until the sealed end is flush with the under side of the stopper, the flask, having a vacuum in the upper part, may be disconnected from the pump and safely heated in the water-bath. The flask must be heated until the reaction is complete (2 hours—2 days), and frequently shaken during cooling, in order to wash down any material which may have sublimed into the upper part of the flask. After standing for a few hours, the picric acid in the filtrate is estimated by titration. Test analyses show that the method is exact, except in the case of β-naphthol, with which a correction must be introduced owing to the solubility of the molecular compound. For every 100 c.c. of picric acid solution, 0.0075 grm. of β-naphthol remains unprecipitated.

Reaction of Solid Hydrocarbons with Metallic Chlorides.—Watson Smith has proposed to employ fused antimonous chloride and bismuthous chloride as reagents for the discrimination of solid hydrocarbons. For this purpose a small quantity of the crystallised chloride is placed in a small porcelain crucible and melted, and then further heated over a small flame. A small particle of the hydrocarbon to be tested is next placed on the side of the crucible, which is then so inclined that the melted chloride comes in contact with it. Fusion follows, accompanied in many cases by a coloration. On restoring the crucible to a vertical position, the coloured spot elongates and forms a coloured streak. Tested in this way, the hydrocarbons give the reactions shown in the following table:

Hydrocarbon	Reaction with antimonous chloride	Reaction with bismuthous chloride
Naphthalene, pure...	No coloration. During cooling, characteristic rhombic tables form in the fused chloride.	No coloration. During cooling, yellow, transparent needles separate.
Naphthalene, impure	More or less carmine coloration.	More or less orange coloration.
Diphenyl...........	No coloration.	No reaction.
Phenanthrene.......	Difficultly soluble. Faint greenish coloration.	Brown or greenish-brown.
Anthracene.........	Traces even give a yellowish-green colour. Colorless needles formed during cooling.	Purple-black coloration, very characteristic.
Dinaphthyls.........	No coloration.	No reaction
Pyrene.............	Same as phenanthrene.	
Chrysene...........	Traces even produce golden-yellow colour.	
Stilbene...........	At 40° smallest trace gives orange colour, destroyed at higher temperature.	
b-Phenylnaphthalene	No reaction.	
Triphenylmethane...	No reaction. Greenish colour with excess.	

Behaviour of Solid Hydrocarbons With Benzal Chloride

E. Lippmann and J. Pollak (*Monatsh.* 1902, **23** (6), 670–671) have devised the following tests:

The colour reactions given in the following table are observed by suspending the hydrocarbons in concentrated sulphuric acid and adding in the cold a few drops of benzal chloride (benzylidene chloride), $C_6H_5CHCl_2$.

Hydrocarbons	Colour	
Anthracene	Malachite green.	
Naphthalene	Magenta.	
Benzene[1]	Light yellow.	Colours varying with the degree of purity.
Toluene[1]	Light yellow.	
Xylene[1]	Orange.	
Phenanthrene	Carmine.	
Triphenylmethane	Faint yellow.	
Picene	Olive-green after a short time.	
Diphenylmethane	Brick-red.	
Stilbene	Bluish-green.	
Pseudocumene[1]	Orange-red.	
Cymol	Orange.	
Pyrene	Emerald-green becoming deep blue.	
Acenaphthene	Dark blue.	
Dibenzylanthracene	Yellowish-green.	
Chrysene	Light yellow, then light green, and finally dark olive-green.	

[1] The hydrocarbons indicated give the same colour with sulphuric acid alone, no alteration taking place on the addition of benzal chloride.

The Valuation of Anthracene.—Commercial crude anthracene is a green or brownish-green friable mass or crystalline powder. It contains a variable percentage of real anthracene, the usual proportions being from 30 to 40%, though sometimes it may contain as little as 15%, and at other times as much as 90%. It cannot be too strongly insisted on that the true value of a crude anthracene is dependent not merely on its real anthracene content, but also on its comparative freedom from objectionable impurities. The three substances to be guarded against especially are paraffins, methylanthracene, and phenylnaphthyl carbazol or phenylnaphthylimid.

Estimation of Paraffin.—The paraffin wax existing in Scotch and north-country anthracenes has a high melting point, and little solubility in either petroleum or coal-tar naphtha. It dissolves in the hot liquids, but is almost entirely deposited on cooling. A small percentage of this paraffin greatly impedes the subsequent treatment of the anthracene, and, being a very stable substance, it passes through most of the processes unchanged. Experience has proved that in the operation of oxidising anthracene on a large scale, by treatment with potassium dichromate and dilute sulphuric acid, all other admixtures may be dealt with and to a great extent removed, but paraffin resists the oxidising action, melts, and retards the operation to a hopeless extent. Hence a search for this objectionable impurity should never be omitted, unless it be known to a certainty that bituminous shale or cannel coal has had no share in the production of the sample. It may be detected and estimated in crude anthracene in the following manner:

10 grm. of the sample are treated with 108 c.c. of strong sulphuric acid. The mixture is heated on a water-bath for about 10 minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin wax will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c.c. of water contained in a tall beaker. After being thoroughly stirred the liquid is allowed to cool, when any paraffin will rise to the surface, and, having solidified, can be removed, washed with a little cold water, dried between blotting paper, and weighed. From 2 to 5% is the quantity commonly present in Scotch anthracenes.

Heusler and Herde (*Zeit. angew. Chem.*, 1895, 253) employ the following method for estimating the paraffin in crude anthracene: 2 grm. of the sample are weighed into a 150 c.c. flask, and fuming nitric acid added slowly—at first, drop by drop—the flask being kept cooled by ice-water. After the mass has been completely digested with the acid the flask is warmed on the water-bath until the undissolved material melts. The mixture is allowed to cool, filtered through asbestos, the filter washed thoroughly with fuming nitric acid, and then with water until a drop of the filtrate gives no turbidity with water. The filter is washed with alcohol and subsequently with warm ether to dissolve the paraffin. The alcohol filtrate is evaporated in a weighed dish, the ether solution added and evaporated, the residue dried for 30 minutes at 105 to 110° and weighed.

The following is a process for estimating small quantities of paraffin in anthracene (*Zeit. angew. Chem.*, 1907, 463). Ten grm. of the anthracene under examination are heated on the water-bath with 108 grm. of strong sulphuric acid until dissolved, and, after cooling, the solution is poured into 400 c.c. of cold water. The mixture is extracted twice with petroleum naphtha, and the extract is washed first with half of its volume of a 5% solution of sodium hydroxide and then four times with one-eighth of its volume of cold concentrated sulphuric acid. It is then washed with water until acid-free, and then distilled from a weighed flask. The residue, multiplied by 10, indicates the percentage of paraffin.

Detection of Phenylnaphthylimide.—According to B. Nickels, samples of crude anthracene containing phenylnaphthylimide show the highly characteristic absorption spectrum of this substance; 2 broad, well-defined black bands between F and G, and another slightly more refrangible than G. Samples exhibiting these bands are purified with some difficulty, and yield by oxidation an impure anthraquinone containing many amorphous particles. For observing the spectrum of the sample, about 1.25 grm. should be dissolved in 6 c.c. of warm benzene, the liquid passed through a dry filter, and observed with a spectroscope. A micro-spectroscope or a direct-vision pocket spectroscope will suffice. The intensity of the absorption-bands is an approximate measure of the objectionable impurities of the sample.

Detection of Methyl-Anthracene.—This very unwelcome substance occurs principally in anthracene prepared from gas-tar obtained in cases where cannel-coal had been used for the making of the gas. If it is present the anthraquinone obtained in the analysis of the anthracene does not appear in the usual needle shape, but as a felted mass. Schultz and Japp (*Ber.*, 1877, **10**, 1050) describe a method for its separation from raw phenanthrene, which consists essentially in the fractional oxidation by means of potassium dichromate and sulphuric acid of the product under examination, distillation, and fractional crystallisation of the distillate from alcohol.

Estimation of Anthracene.—For the quantitative valuation of commercial anthracene the most satisfactory method is that based on the formation of anthraquinone by the action of chromic acid. This is a characteristic, insoluble substance, not liable to further change, while nearly all the associates of anthracene are, by the same treatment, either completely oxidised or else converted into products readily removed by water or dilute alkali.

This method was first proposed by E. Luck, and, with suitable modifications, affords a very satisfactory solution of a difficult problem. The following mode of operating is essentially that of Meister, Lucius, and Brüning, with some precautions and modifications recommended by G. E. and T. H. Davis, who verified the accuracy of the method by operating on pure anthracene and impure samples of known composition. The test is commercially known as "Meister, Lucius, and Brüning's anthraquinone test, with appendix." 1 grm. of the carefully sampled specimen is placed in a flask of 500 c.c. capacity. 45 c.c. of the very strongest glacial acetic acid are then added, and an inverted condenser or long glass tube adapted to the flask. The liquid is then brought to the boiling point, and while boiling, the chromic acid is added to it gradually, drop by drop, by means of a tapped funnel passing through the india-rubber stopper of the flask, or inserted in the top of the vertical condenser. The chromic acid solution is prepared by dissolving 15 grm. of crystallised chromic anhydride (perfectly free from lead salts and insoluble matter generally) in 10 c.c. of water and 10 c.c. of glacial acetic acid. The addition of the oxidising agent should occupy two hours, and the contents of the flask should be kept in continued ebullition for two hours longer, four hours in all being necessary to ensure complete oxidation of the impurities. The flask is then left at rest for twelve hours, when the contents should be diluted with 400 c.c. of cold water and allowed to rest another two hours. The precipitated anthraquinone is then filtered off and well washed with cold water. It is next washed on the filter with a boiling-hot 1% solution of sodium hydroxide, and again thoroughly washed with boiling water, about 300 c.c. being employed. The anthraquinone, which should exhibit no alkaline reaction, is then rinsed from the filter into a small dish by means of a jet of water, the water evaporated, and the residue dried at 100° and weighed.

The anthraquinone obtained in the foregoing manner is rarely sufficiently pure to allow of the percentage of real anthracene in the sample being at once calculated from its weight. Several methods have been proposed for the further purification of the crude product, but the following improved "appendix" by Meister, Lucius, and Brüning, commercially known as the "sulphuric acid test of October, 1876," is now universally employed. The crude anthraquinone is mixed in the dish in which it was weighed, with 10 times its weight of fuming sulphuric acid having a sp. gr. of 1.880 at 60° F., and the whole heated to 100° on a water-bath for ten minutes. The solution obtained is next left in a damp place for 12 hours to absorb water. 200 c.c. of cold water are then added, the precipitated anthraquinone collected on a filter, and washed free from acid with cold water, then with about 100 c.c. of boiling sodium hydroxide solution (1%), and finally with about 400 c.c. of boiling water. The character of the quinone is an indication of its purity, a deep yellow or orange tint indicating the presence of phenanthrene- or chrysene-quinone. The latter substance is also recognised by the production of an indigo-blue coloration on adding the sulphuric acid. With impure anthraquinones both the acid filtrate and the alkaline washings are deeply coloured—brown, purplish, and bluish tints being the most common.

The greater part of the moist anthraquinone is then transferred to a flat platinum or porcelain dish by means of a spatula, the remaining portion being rinsed off the filter into the dish by means of a fine jet of water. The water is then evaporated at 100°, and the residue weighed. An alternative method is to dry the anthraquinone on the filter, and then remove it. To avoid loss, the stained portion of the filter may be cut small and heated in a test-tube with about 1 c.c. of benzene. The resulting solution is poured off into a small dish, and the residue obtained by its evaporation added to the main quantity of anthraquinone. The difference in the result caused by the benzene treatment often amounts to 0.2% of the crude anthracene, owing to the loss in other methods by imperfect removal from the filter. Hence, when the analyst is not limited by the conditions of the contract note, treatment of the filter with benzene should not be neglected. Either of the foregoing methods of treatment is preferable to weighing the anthraquinone on the filter, which is apt to be altered in weight by the reagents employed, though this source of error may be to a great extent avoided by using a double filter, the apex of the outer one being cut off. The weights of the two filters are accurately adjusted before use by trimming with a pair of scissors, and on weighing the anthraquinone, the outer filter is used as a counterpoise to the inner.

H. Bassett (*Chem. News*, 1896, 73, 178) has proposed the following modification of this method: after the washing of the anthraquinone collected on the filter, it is dried in the water-oven and then transferred to a flask of the usual size, with a short and wide neck, a small wash-bottle containing 45 c.c. of glacial acetic acid being used to rinse the filter-paper and funnel. (The hardened filter-paper now available would probably serve well.) 10 c.c. of pure nitric acid (sp. gr. 1.4) and 2.5 c.c. of chromic acid solution are added, and the mixture boiled for an hour, beneath a reflux condenser. The flask is allowed to stand overnight, its contents then diluted to 400 c.c., filtered, and the residue washed with water, and then with boiling solution of sodium hydroxide as above. Bassett (*Chem. News*, 1895, **71**, 202) states that samples of chromic anhydride often contain considerable sulphuric acid, but this does not interfere seriously with the test.

The weight of anthraquinone thus obtained ought not to be regarded as representing that of the pure product, as it usually contains extraneous matters, such as sand, and frequently chromium. Some anthracenes yield anthraquinones which carry much chromium sesquioxide. Hence the dish should be gradually heated so as to completely sublime the anthraquinone, and the residue obtained deducted from the weight previously found. This corrected weight of the anthraquinone, multiplied by the factor 0.856, gives the real anthracene in the weight of the sample employed.

The anthraquinone obtained by the above process should be crystalline and of a uniform pale-yellow colour. The purer it is, the paler the colour. Certain strange quinones are apt to be present in some cases, and are recognisable by the modified form of the crystals and the colour of the product. Phenanthraquinone is orange, and chrysene-quinone deep red. Continued treatment with the chromic acid mixture removes all these substances, but does not affect the quinone, $C_{16}H_9NO_2$, produced by the oxidation of imido-phenylnaphthyl referred to on page 263 as giving a characteristic absorption-spectrum. This substance, unlike the quinones from phenanthrene, chrysene, etc., tends to prevent the crystallisation of the anthraquinone, and is one of the sources of the so-called "amorphous particles" which are frequently present in sufficient quantity to obliterate all trace of crystallisation in the oxidised product. This troublesome impurity may, however, be destroyed by a somewhat longer-continued heating with sulphuric acid in the manner already described, and hence this supplementary treatment should never be omitted in the case of samples which originally showed absorption-bands, or which have produced crude anthraquinones of abnormal appearance.

For the estimation of anthracene in coal-tar, C. Nicol (*Ztschr. anal. Chem.*, 1875, 318) distills twenty grm. in a small luted retort, and the vapours are received in a U-tube, kept at 200° by being immersed in a bath of hot paraffin. The more volatile products are not condensed, but the anthracene and other hydrocarbons of high boiling point collect in the U-tube. Care must be taken to prevent bumping and the condensation of the distillate on the neck and sides of the retort. When the contents of the retort become coked, the process is stopped and the neck is cut off, pounded, and the powder added to the distillate. The whole is then dissolved in glacial acetic acid, and subjected to oxidation with the chromic acid mixture in the manner already described. Watson Smith considers twenty grm. far too small a quantity. He operates on at least a liter, and rejects the portion distilling just before coking, as it contains much resinous matter of an objectionable kind, and would not in practice be treated for anthracene. The anthracene oil is well mixed and an aliquot part oxidised.

In some cases it is preferable to reject the fraction distilling between 200° and 250° as it contains little or no anthracene, and in tars rich in naphthalene is so large in quantity as materially to impede the subsequent treatment. The anthracene may be further concentrated by cooling the heavy oils to a low temperature, filtering, and pressing the deposit of solid hydrocarbons between folds of filter paper. The crude anthracene thus obtained is then oxidised to anthraquinone in the usual way. Ordinary gas-works coal-tar contains from 0.3 to 0.5% of real anthracene, but from the tar obtained from Simon-Carvès coke-ovens Watson Smith obtained 0.73% of anthracene, and A. H. Elliott found as much as 2.63% in the tar produced in the manufacture of water-gas from petroleum naphtha.

Detection of Carbazol and Phenanthrene:—Carbazol and phenanthrene in anthracene are detected, according to H. Behrens (*Chem. Centr.*, 1902, **2**, 540), as follows: the sample is extracted in the cold with acetic ester, the solution allowed to evaporate, and the residue transferred by the aid of a few drops of the same solvent to a watch glass. On evaporation the carbazol is left behind; when treated with a drop of nitro-benzene and phenanthraquinone, it yields characteristic small copper-coloured plates. Phenanthrene is detected by extracting with benzene and treating the evaporation residue of the extract with a di-nitrophenanthraquinone dissolved in nitrobenzene.

Estimation of Carbazol.—The carbazol content of anthracene is best obtained by first washing the sample of anthracene under examination with dilute sulphuric acid for the removal of acridine which may be present, and then estimating the nitrogen by the Kjeldahl method. From this the carbazol content can readily be calculated.

Estimation of Phenanthrene.—The determination of phenanthrene is more difficult than that of anthracene and carbazol. Lunge (*Coal Tar* and *Ammonia*, Vol. II, 643) states that the following method gives fairly reliable results only in the case of a material rich in phenanthrene. For estimating it in crude anthracene the percentage of phenanthrene is increased as follows: dissolve 1 kgm. crude anthracene in 2 kgm. toluene and allow the solution to crystallise at the ordinary temperature, with frequent stirring, for six hours. Separate the liquor after drawing it off by a vacuum pump and washing with 200 c.c. toluene from the anthracene and carbazol, which had been separated as crystals, and remove the toluene by evaporation. The residue thus obtained is submitted to fractional distillation, and the product passing over between 280° and 340° is considered as crude phenanthrene and treated as follows: 20 grm. of it are heated with a solution of 30 grm. picric acid in 300 c.c. dry xylene in a flask with reflux cooler. The crystals separated after standing for twenty-four hours, during which time the mass should be strongly shaken up several times, are collected on the vacuum pump, dried, and weighed as crude picrate. The mother liquor is diluted with 50 c.c. xylene, and in it once more 20 grm. crude phenanthrene and 30 grm. picric acid are dissolved. The difference between the quantity of crude picrate now obtained against the weight of the first crop of crystals shows the crude picrate dissolved in 250 c.c. xylene. From the solubility factor thus obtained and the weights of the crops of crystals the total weight of the rough picrate formed from 40 grm. of the crude phenanthrene is found. A weighed portion of this is recrystallised from 95% alcohol. To the weight of the pure picrate, separating in the shape of shining yellow-red needles, that dissolved in the alcohol (20 grm. for 750 c.c. 95% alcohol) must be added. It is better to convince one's self of the purity of the last-obtained picrate, by decomposing it with ammonia, washing the hydrocarbon with dilute sulphuric acid (to remove any acridine possibly present), and weighing the remainder; 100 picrate = 43.7 phenanthrene. In the case of very impure phenanthrene it is preferable to work upon 30 grm. each time, allowing 45 grm. picric acid and 200 c.c. xylene (in lieu of 50 c.c.) after the first crystallisation. The difference of both crystallisations now represents the solubility of crude picrate in 100 c.c. xylene.

Estimation of Anthraquinone.—Lewis (*J. Ind. Eng. Chem.*, 1918, **10**, 425) has developed the following method for the estimation of anthraquinone and has shown that a quantitative separation of this compound from anthracene and comparatively small amounts of phenanthraquinone is possible. The method is based on the fact that anthraquinone, when warmed with zinc dust and alkali, passes into anthrahydroquinone, the sodium salt of which is soluble in water, forming a solution with a red colour.

One part of anthraquinone is wet with a small quantity of alcohol, mixed with 2 parts of zinc dust, and about 50 parts of a hot 5% sodium hydroxide solution added. The mixture is heated just below the boiling point for 5 minutes, and then rapidly filtered by suction, and the residue washed once with water. The filter paper with the residue is heated with another equal portion of the sodium hydroxide solution, and the liquid rapidly filtered into the same flask. A third heating with alkali is sufficient to effect the solution of any residue of anthraquinone that may remain unreduced. The combined filtrates are cooled and reoxidised by shaking in the presence of air. A practical procedure is to shake the suction flask under a stream of cold water until the red colour disappears. The resulting anthraquinone is filtered upon a weighed Gooch crucible, washed with water, dried at 110° and weighed.

The following precautions must be observed:

If the mixture is boiled for too long a period, there is some formation of the next reduction step, the compound known as anthranol, which contains one atom of oxygen less than does the oxanthranol, and does not reoxidise to anthraquinone by the action of air. The presence of this compound is easily shown by any yellow colour in the filtrate from the final reoxidation.

There is danger that all the anthraquinone may not go into solution through the reduction. This is readily determined. If the residue on the third filter paper imparts no red colour to the liquid when boiled again with hot alkaline solution, the reduction is complete.

A green colour showing in the reoxidised anthraquinone indicates the presence of a reduced compound of phenanthraquinone, the structure of which has not been determined. Phenanthraquinone in the original substances causes high results, but when present in amounts less than 10% the error is not sufficient to vitiate the practical value of the method.

It is necessary that the hot solution of the reduced anthraquinone be filtered rapidly in order to prevent reoxidation on the filter.

It has been found that certain grades of asbestos are affected by alkali, and it is necessary that the asbestos, before use, should be freed from alkali-soluble constituents.

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PHENOLS

J. BENNETT HILL, PH. D.

The substances termed phenols are intermediate in character between acids and the true aromatic alcohols, of which benzyl alcohol is the type.

The monohydric phenols have the general formula $C_nH_{2n-7}OH$. Of these, phenol and cresol are described in the following sections. Thymol, $C_{10}H_{13}OH$, which is a higher homologue of these bodies, will be considered in connection with the essential oils. The naphthols, $C_{10}H_7OH$, which are closely related to the monocyclic phenols, are described on page 227.

The dihydric phenols or hydroxyphenols, $C_nH_{2n-8}.(OH)_2$, are described on page 332. Catechol (or pyrocatechin), resorcinol, and quinol (or hydroquinone) are isomeric substances of the formula $C_6H_4(OH)_2$. Orcinol, or orcin, $C_7H_6(OH)_2$, obtained from various lichens, is a phenol homologous with resorcinol.

The trihydric phenols or dihydroxyphenols are represented by pyrogallol and phloroglucinol, $C_6H_3(OH)_3$.

Certain ethers of catechol and pyrogallol are described in the section on "Wood Creosote" (page 300), in which liquid they are present in large proportion.

MONOHYDRIC PHENOLS. $C_nH_{2n-7}OH$

The monohydric phenols form a homologous series, of which phenol proper, or carbolic acid, is the first member, the cresols form the next homologue, and the xylenols the next.

Of the higher members of the series, some exist in the tars produced by the distillation of coal and wood; others in certain natural essential oils (*e.g.*, thymol); while others have hitherto been obtained by synthetical reactions only.

The monohydric phenols may be regarded as being formed from benzene and its homologues by the substitution of a molecule of hydroxyl for an atom of hydrogen in the principal chain. All but the lowest term are susceptible of isomeric modifications, according to the relative positions of the hydroxyl and other substituted radicals in the benzene nucleus.

Phenol and its higher homologues are closely related in properties. They are very stable compounds, subject to fairly ready purification and may be distilled without decomposition. Above their melting points and in a pure state they are colourless highly-refractive liquids with a tendency to darken on exposure to light and air. When highly purified this tendency is less marked.

The phenols are weak acids, dissolving in alkalies with replacement of their hydroxyl hydrogen by metal, to form salts known as phenolates or carbolates. They are all more weakly acid in their properties than carbon dioxide, being liberated from solutions of their salts by the action of this gas. Phenol is the most strongly acid of the series, the acidities falling off with increasing molecular weights. Phenol in aqueous solution shows a dissociation constant of about 1×10^{-10} at 25°.

The phenols are readily soluble in alcohol, ether, chloroform, carbon bisulphide, benzene, carbon tetrachloride and glycerin. Whilst phenol is fairly soluble in water, the solubilities of the higher homologues in water fall off very rapidly with increase in molecular weight. The phenols show a moderate solubility in the petroleum solvents at normal temperatures.

The phenols are bactericidal and toxic. The bactericidal property rises with increase in molecular weight, whilst the toxicity falls off. A substitution of nuclear hydrogen by halogen increases both the bactericidal value and the toxicity. The phenols are also corrosive to the skin, this property becoming much less marked in the higher homologues.

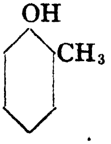
The melting points show no regular relationship, whilst the boiling points rise with molecular weight. A tabulation of these constants for the lower members is shown below:

	M. P.	B. P.	Sp. Gr. 25°
Phenol	40.8°	182.6°	1.0584 (40°)
o-Cresol	30.6	191.4	1.0449
p-Cresol	36.0	201.8	1.0334
m-Cresol	11.0	202.3	1.0335
Xylenols	....	211–225	......

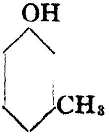
The monohydric phenols are isomeric with the true aromatic alcohols, such as benzyl alcohol, in which the hydroxyl group is present not in the nucleus but attached to carbon in the side chain. The relation between the four isomers having the empirical formula C_7H_8O is shown below:

Varieties of cresol or methyl-phenol.

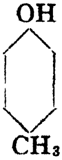
Orthocresol (1–2)



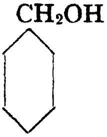
Metacresol (1–3).



Paracresol (1–4).



Benzyl alcohol or phenyl-carbinol.



The monohydric phenols are distinguished from the *alcohols of the benzyl series* by the following reactions:

(*a*) Hydrochloric acid is without action on the phenols, but (*e. g.*) converts benzyl alcohol into benzyl chloride, $C_6H_5CH_2Cl$.

(*b*) Phenol readily dissolves in concentrated sulphuric acid to form phenolsulphonic acids, whilst benzyl alcohol is resinified by similar treatment.

(*c*) On treatment with oxidising agents the phenols yield quinones, but benzyl alcohol yields benzoic acid.

(*d*) Nitric acid converts the phenols into well-characterised nitro-derivatives of acid character, but benzyl alcohol is oxidised by the same reagent to benzoic aldehyde and benzoic acid.

(*e*) The phenols dissolve in solutions of alkalies to form compounds in which they play the part of an acid. The acid character is less marked in the higher members of the series, but the chloro- and nitro-derivatives have strongly acid properties, not only dissolving in solutions of alkaline hydroxides, but decomposing carbonates with effervescence and forming definite and stable salts.

(*f*) Ferric chloride produces a characteristic blue or violet colour with many of the phenols and their derivatives.

(*g*) On adding hydrochloric acid to the aqueous solution of a phenol, immersing a slip of pine-wood and allowing it to dry, a blue colour is developed.

(*h*) The phenols react immediately with excess of bromine water to form bromo-derivatives (usually containing Br_3), which are usually white or yellowish, and are insoluble or nearly insoluble substances.

The reactions of the phenols of service for their recognition are described more in detail on page 280.

PHENOL. CARBOLIC ACID

Hydroxybenzene C_6H_5OH

The principal natural source of phenol is the fraction from the distillation of coal tar commonly known as the "carbolic oil" fraction and having a distillation range of approximately 150–300°. For the recovery of phenol from this fraction the oil is treated with a solution of sodium hydroxide, when the phenol and its homologues are extracted from the oil and dissolved in the soda solution as phenolates. This solution is carefully separated from the oil and the phenols or tar acids liberated with sulphuric acid or carbon dioxide. The crude product which separates is fractionally distilled to give a crude phenol which is generally finally purified by partially crystallising and separating the pure crystals from the impure mother liquor. The other fractions from the fractional distillation of the crude tar acids are the source of the higher phenol homologues.

Phenol is also manufactured synthetically. The only commercially important process for its production consists in sulphonating benzene to the benzene-mono-sulphonic acid, separating this from the unused sulphuric acid, neutralising it to its sodium salt, and fusing it with sodium hydroxide. Sodium phenolate and sodium sulphite are formed according to the following reaction:

$$C_6H_5SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O.$$

The melt is dissolved in water, and the phenol liberated with sulphuric acid or carbon dioxide and purified by distillation. A very good grade of phenol is obtained by this method. The various processes for the production of synthetic phenol all follow this general procedure, the principal differences from each other being in the method of obtaining the sodium benzene sulphonate free from sodium sulphate.

A good grade of phenol may be prepared in the laboratory by the dry distillation of salicylic acid or sodium salicylate with lime.

Pure phenol is a colourless solid crystallising in long orthorhombic prisms. Its melting point is variously reported as 40.8° to 42.1°. The 40.8° figure is generally accepted as the true m. p. of phenol, as shown by its freezing point. The m. p. is very rapidly depressed by the presence of water. Solid phenol at 0° has a sp. gr. of 1.084. Above its m. p. phenol is a mobile colourless liquid with a sp. gr. of 1.0584 at 40°. It boils at 182.6°. Phenol has an astringent, but sweetish taste, and a very characteristic odour which is much less pronounced in the highly purified material. The synthetic product frequently has a very rank odour due to traces of thiophenol.

The United States Pharmacopœia (ninth Edition, 1916) contains the following description of phenol of medicinal purity:

"Phenol occurs in colourless, interlaced, or separate needle-shaped crystals, or as a white, crystalline mass, sometimes acquiring a red tint; having a characteristic, somewhat aromatic odour. When undiluted it cauterises and whitens the skin and mucous membrane.

"1 grm. of Phenol dissolves in about 15 mils of water at 25°.; very soluble in alcohol, glycerin, chloroform, ether, carbon disulphide, or in fixed or volatile oils.

"An aqueous solution of Phenol (1 in 15) is clear and neutral or at most only faintly acid to litmus.

"When gently heated Phenol melts, forming a highly refractive liquid. It is also liquefied by the addition of about 8% of water.

"Congealing point: not below 38°.

"Its aqueous solution yields with bromine water a white precipitate of tribromphenol, which at first redissolves, but becomes permanent as more of the reagent is added, and appears crystalline when viewed under the microscope.

"Add 1 drop of ferric chloride T. S. to 1-mils of an aqueous solution of Phenol (1 in 100); the liquid acquires a violet-blue colour.

"Heat about 10 grm. of Phenol on a water bath; it is volatilised without leaving more than 0.05% of residue. The vapour is inflammable."

Phenol is somewhat soluble in water and water in phenol. At temperatures below 68.3° a mixture rich in both water and phenol separates into two layers, the lower layer being a solution of water in phenol and the upper layer a solution of phenol in water. Above 68.3° phenol and water are miscible in all proportions. The solubility relations are shown in the following table:

t°	Grm. phenol per 100 grm.	
	Aqueous layer	Phenol layer
10°	7·5	75 0
20	8.3	72.1
30	8.8	69.8
40	9.6	66.9
50	12.0	62.7
55	14.1	59·5
60	16.7	55·4
65	21.9	49·2
68 3	33·4	

Phenol is much less soluble in solutions of sodium chloride, sodium sulphate, calcium chloride and other similar inorganic salts.

Phenol forms a hydrate with water, corresponding to the formula, $2C_6H_5OH.H_2O$. This hydrate has a m. p. of 15.9°, but is very difficult to crystallise unless the mixture is seeded with crystals of the hydrate.

Phenol coagulates albumin, is a powerful antiseptic, acts as a caustic on the skin, and is powerfully *poisonous*. Its local action is much influenced by the solvent; it is stated that the solution in pure glycerol or absolute alcohol is scarcely caustic.

Phenol burns on the skin should be washed *freely* with alcohol as soon as possible and treated subsequently as ordinary burns. Small burns on the hands caught immediately before the skin is much attacked may be treated by rubbing the spot thoroughly with a fairly strong solution of caustic soda and washing with water.

Strong phenol dissolves gelatin completely, but coagulates it when added to its aqueous solution. Indigo-blue (indigotin) is soluble in hot phenol and may be obtained in crystals on cooling the liquid.

By the action of fused sodium hydroxide on phenol, phloroglucinol, catechol, and resorcinol are formed, together with other products.

Phenol is converted by the action of chlorine and bromine into chloro- and bromo-derivatives. Nitric acid acts on it with formation of nitrophenols. Concentrated sulphuric acid converts phenol into phenolsulphonic acids. Hydrogen dioxide converts phenol into catechol, hydroquinone, and quinone.

Phenol on standing turns red. There is much difference of opinion as to the cause of this discoloration. It is undoubtedly hastened by the presence of small quantities of iron salts or by traces of alkali, even such as may be dissolved from a glass bottle. Gibbs (*Philippine J. Sci.*, 3, 361) maintains that the reddening is due to traces of dissolved oxygen, water and light.

An aqueous solution of pure phenol does not affect litmus or phenolphthalein.

Phenates

Phenol dissolves in alkalies to form compounds known as phenates, phenolates or phenoxides, in which the hydroxyl hydrogen is replaced by metal. The phenates are decomposed by acids including carbon dioxide. Sodium phenate, C_6H_5ONa, and potassium phenate, C_6H_5OK, may be readily crystallised from their solutions. Calcium phenate, $(C_6H_5O)_2Ca$, is easily formed by dissolving phenol in milk of lime and is quite soluble in water. On boiling its aqueous solution half the phenol is liberated and the basic salt, C_6H_5OCaOH, is precipitated.

Phenol acts readily on metallic lead and dissolves aluminium at its boiling point. It has an appreciable action on copper, the copper salt being very highly coloured. Zinc, tin and iron are scarcely attacked.

Phenol Ethers and Esters

Phenol, like the aliphatic alcohols, forms both ethers and esters.

On heating potassium phenate with alkyl iodides, ethers are produced. *Methyl phenate*, or anisole, $C_6H_5OCH_3$, is a mobile liquid of pleasant, aromatic odour, having a density of 0.991 and distilling unchanged at 152°. It dissolves in strong sulphuric acid to form anisolsulphonic acid, and with bromine yields substitution products. Ethyoxybenzene, phenetole, and amyl phenate resemble the methylic ether.

Besides the foregoing substances, which are of the type of the mixed ethers, many phenol esters are known, but have little practical importance. The production of phenol orthoxalate has been observed to occur in the manufacture of aurin; phenyl salicylate constitutes the antiseptic known commercially as "salol."

Qualitative Tests for Phenol.—The following reactions are in most cases common to phenol and the cresols. They do not require that the substance should be in a concentrated state, but are applicable to the aqueous solution.

(*a*) When a drop of a dilute aqueous solution of phenol is added to a few drops of a solution of 1 grm. of molybdic anhydride in 10 c.c. of concentrated sulphuric acid, contained in a porcelain crucible, a yellowish-brown spot is produced, which rapidly changes to purple, the latter tint being tolerably permanent. Warming the mixture to about 50° greatly assists the reaction, but a higher temperature must be avoided. As this test depends on the deoxidation of the molybdic anhydride, many substances interfere with it.

(*b*) Ferric chloride (avoiding excess) gives a fine violet colour, by which 1 part of phenol in 3,000 of water can be detected. Many allied substances give a similar reaction. The presence of common salt, nitre, or boric acid is unobjectionable, but the reaction is hindered by most mineral and organic acids, acetates, borax, sodium phosphate, glycerol, alcohol, amyl alcohol, and ether.

(*c*) If an aqueous solution of phenol be gently warmed with ammonia and a solution of sodium hypochlorite (avoiding excess), a deep-blue colour is obtained, which is permanent, but turns to red on addition of acids. Solutions containing 1 part of phenol in 5,000 of water react well when 20 c.c. are employed. Much smaller quantities give the reaction after a time.

A modified, and in some respects preferable, method of performing the test is to add to 50 c.c. of the aqueous liquid to be tested 5 c.c. of a mixture of 1 measure of ammonium hydroxide of 0.880 sp. gr. with 9 measures of water, and then drop in fresh and dilute bromine-water very slowly, avoiding excess. The presence of phenol will be indicated by the production of a fine blue tint, which is very permanent. A still better plan is to expose the ammoniacal liquid to the vapour of bromine, avoiding excess of the latter.

(*d*) When bromine water is added in moderate excess to an aqueous solution of phenol, a snow-white crystalline precipitate is formed, which readily collects into flocks on agitation, and appears under the microscope in the form of fine stellated needles. In presence of much cresol or of certain other phenols the precipitate loses its crystalline character, and may even assume the form of yellow or reddish oily globules. In extremely dilute solutions the precipitate is only produced slowly; but in 24 hours a solution containing 1/60,000 of phenol gives the reaction.

The reaction with bromine is by no means conclusive evidence of the presence of phenol, a similar reaction being produced by homologues of phenol (*e. g.*, cresol, thymol), besides other phenolic substances (*e. g.*, guaiacol, orcinol, pyrogallol, phloroglucinol), salicylic acid, aniline, and various alkaloids.

(*e*) A dilute solution of phenol treated with 10 c.c. N/10 iodine solution and 10 c.c. N/10 sodium carbonate, followed after five minutes by acidification with sulphuric acid, gives a reddish precipitate of triiodophenol and tetraiododiphenylenequinone. In extremely dilute solution the reaction develops slowly after acidification. The reaction is claimed by Wilkie to be delicate to one part of phenol per 1,250,000 parts of water. Salicylic acid and other phenolic substances give similar reactions.

(*f*) If 20 c.c. of a dilute phenol solution are boiled with 5 or 10 drops of Millon's reagent (prepared by dissolving mercury in an equal weight of fuming nitric acid, boiling, diluting the solution with 2 volumes of water, and adding nitric acid drop by drop to the hot solution, until the precipitate is redissolved), the mixture assumes a fine blood-red colour, which is permanent for several days. The reaction is exceedingly delicate, but is not peculiar to phenol.

E. Ackermann (*Rev. Chim. Ind.*, 1895, 322) obtained the following results when 0.01 grm. of the phenolic substance was acted on by about 20 drops of Millon's reagent: Beechwood creosote gave a reddish-brown coloration in the cold, the colour remaining unaltered after 15 minutes' standing. On heating, the colour changed to brownish-black. Creosol and guaiacol both gave a red coloration in the cold, changing to reddish-brown after 15 minutes. On heating, the colour became brownish-black. Resorcinol gave an orange coloration in the cold, unchanged after 15 minutes, but changed to deep-red on heating. α-Naphthol gave an immediate red coloration in the cold, and β-naphthol gave a brown coloration on heating. Proteins, some morphine compounds, and various other substances also give with this reagent colorations which are often very similar to those given by phenoloids.

E. Hoffmann modifies this test by pouring 2 or 3 c.c. of the liquid supposed to contain phenol onto the surface of an equal volume of strong sulphuric acid, so as not to cause the liquids to become mixed.

A few granules of potassium nitrite are then dropped in, when each particle will produce violet streaks, if even a very minute quantity of phenol be present.

Liebermann has observed that strong sulphuric acid to which a 6% solution of potassium nitrite has been added gives a brown coloration, changing to green and blue when gently warmed with phenol or its allies.

(*g*) The phenols give characteristic colour-reactions with chloroform and alkali. The phenol is dissolved in chloroform, a small piece of potassium hydroxide added, and the solution boiled. The characteristic coloration is quickly developed. Reducing and oxidising agents affect the reaction, alcohol sometimes accelerates and sometimes hinders it, ether nearly always impedes it. In aqueous solutions the reaction is less sharp; in this case it is best to shake up with chloroform and proceed with the decanted chloroform as usual, or to extract with ether, boil the ether off, and dissolve the residue in chloroform. When testing for phenols in complex liquids, such as blood or the contents of a stomach, it is best to acidify and distil in a current of steam. The distillate may then be examined as above.

The results of the test with some members of the phenol group are given below. The following additional data relate to the behaviour of substances not likely to be found in food or beverages when subjected to the foregoing test (Abst. *J. Soc. Chem. Ind.*, 1890, 974):

Metacresol.—As with orthocresol, but a more marked orange shade.

Thymol.—Fine red coloration verging on purple, with a violet tinge, which is accentuated by the addition of a little alcohol or ether, and soon disappears. Limit of sensitiveness, 1:20,000.

Guaiacol.—Cherry-red coloration with a blue tinge, changing to violet-blue. Limit of sensitiveness, 1:100,000.

Resorcinol.—On warming gently, a cherry-red deposit on the potash and a brownish-yellow coloration of the chloroform; the chloroform ultimately takes up the colour, which is fairly stable. Limit of sensitiveness, 1:500,000.

Quinol.—Bluish-green coloration, soon disappearing. Limit of sensitiveness, 1:20,000.

Pyrogallol.—A reddish-brown coloration in the cold, which on warming takes on a green tinge, and on boiling soon disappears. Limit of sensitiveness, 1:300,000.

(*h*) According to J. Moir (*Chem. News*, 1922 **124**, 245) a diazotised solution of *p*-nitraniline hydrochloride can be used to detect one part per million of phenol. 1.5 grm. *p*-nitraniline is dissolved in 500 c.c. water and 40 c.c. hydrochloric acid. The solution to be tested is neutralised and 0.5 grm. sodium acetate added. 5 c.c. of the reagent is treated with sodium nitrite until colourless and added to the liquid to be tested. After 1 minute, an excess of sodium hydroxide solution is added. Phenol gives a ruby red colour, cresols rose-pink, naphthol blue, etc. The various phenols can be identified by the positions of the absorbtion bands.

Estimation of Phenol.—Phenol, where possible, is commonly estimated by the Koppeschaar method, or some modification of it. This method makes use of the precipitation of phenol as tribromophenol by means of bromine solution, the excess bromine being estimated iodometrically. The method when properly run gives very satisfactory results. The details as recommended by Redman, Weith and Brock (*J. Ind. Eng. Chem.*, 1913, **5**, 389) are as follows:

A N/10 bromine solution is prepared by dissolving 2.76 grm. potassium bromate and 15 grm. potassium bromide in water, diluting to 1,000 c.c., and standardising against N/10 sodium thiosulphate (2.48 grm. per liter) by adding acid and potassium iodide and titrating the liberated iodine. The thiosulphate may be checked against N/10 potassium dichromate with acid and potassium iodide.

The phenol to be tested is made up to a solution of N/10 or less. 15 c.c. of this solution is mixed with 50 c.c. of water and 5 c.c. concentrated hydrochloric acid in a 500 c.c. glass stoppered bottle. The N/10 bromine solution is run in from a burette with constant shaking until a permanent pale yellow colour is obtained. The temperature during this addition should be about 22°. The bottle is stoppered and shaken for 1 minute, 0.5 c.c. of 20% potassium iodide solution is added and the shaking continued for 1 minute more. The free iodine is titrated back with N/10 sodium thiosulphate solution using starch solution as indicator and titrating till disappearance of the blue colour. The bromine solution consumed is the original volume added, minus that corresponding to the volume of thiosulphate solution used in titrating back. 1 c.c. of N/10 bromine solution is equivalent to 0.0015675 grm. of phenol.

An iodometric method for the estimation of phenol was suggested by Messinger and Vortman. A practical method based on this has been worked out by Wilkie and still further modified by Redman, Weith, and Brock (*J. Ind. Eng. Chem.*, 1913, **5**, 831). The method is based on the action of iodine on the phenol in weak alkaline solution with the formation of triiodophenol. This light coloured compound on standing changes over to red tetraiododiphenylenequinone with the elimination of hydriodic acid. Whilst this does not affect the titration, it does obscure the end point and the modified method is designed to eliminate its formation. The method is as follows: the sample to be tested is diluted to about N/10 and 15 c.c. of this solution added to 50 c.c. water and 50 c.c. N. sodium hydrogen carbonate solution in a 500 c.c. glass stoppered bottle. A N/30 solution of iodine is run in until the alkaline iodine colour is produced and then continued to about 20% excess. The bottle is stoppered and shaken continuously for 1 minute. 50 c.c. 2 N. sulphuric acid is now added, the mixture shaken and titrated back immediately with N/10 sodium thiosulphate solution using starch as indicator. The estimation should be carried out at 20–25°. Six atoms of iodine are equivalent to one of phenol or 1 c.c. of exactly N/30 iodine is equivalent to 0.0005225 grm. phenol. The method is applicable also to the three cresols, meta-cresol forming a triiodo compound and ortho- and para-cresols diiodo compounds.

The United States Pharmacopœia (9th revision, 1916) gives the following method: "dissolve about 1.5 grm. of the Phenol to be assayed, accurately weighed, in sufficient distilled water to make 1,000 mils. Transfer an aliquot portion of this solution, containing not less than 0.038 grm. nor more than 0.041 grm. of Phenol, to a 500 mil glass-stoppered flask having a long, narrow neck, add 30 mils of N/10 bromine V. S., then 5 mils of hydrochloric acid and immediately insert the stopper. Shake the flask repeatedly during half an hour, allow it to stand for 15 minutes, remove the stopper just sufficiently to introduce quickly 5 mils of an aqueous solution of potassium iodide (1 in 5), being careful that no bromine vapour escapes, and at once stopper the flask. Shake the latter thoroughly, remove the stopper and rinse it and the neck of the flask with a little distilled water, so that the washings may flow into the flask, then add 1 mil of chloroform, shake the mixture well and titrate with N/10 sodium thiosulphate V. S., using starch T. S. as indicator. It shows not less than 97% of C_6H_5OH.

"Each mil of N/10 bromine V. S. corresponds to 0.001568 grm. of C_6H_5OH. Each gram of Phenol corresponds to not less than 618.6 mils of N/10 bromine V. S."

In the manufacture of synthetic phenol it is frequently desired to determine phenol in the presence of sodium sulphite. This salt would interfere with either the bromine or iodine titrations. To meet this need J. M. Weiss has developed a method based on the precipitation of tribromophenol and its titration acidimetrically. This method as used by the Barrett Company is as follows: a suitable sized portion (containing about 0.01 grm. phenol) of the solution to be analysed is taken in a beaker and acidified with hydrochloric acid. The solution is diluted to about 200 c.c. and bromine water added until a permanent yellow colour appears. Excess bromine is destroyed by an excess of strong $NaHSO_3$, the solution being stirred very thoroughly during the addition. The mixture at this point should be pure white. In exceptional cases, however, a slight brown colour is observed which cannot be destroyed by further addition of bisulphite solution. This does not however appear to interfere. The solution is acidified again with hydrochloric acid and the tribromophenol filtered on a Gooch crucible, using a circle of hardened filter paper as the filter medium. Care should be taken during the filtration that the contents of the crucible is not allowed to be sucked dry. If this occurs, the tribromophenol cakes and filtration becomes very nearly impossible. The tribromophenol is carefully washed with a saturated solution of NaCl until the filtrate fails to show acidity. The filter flask is now changed and the tribromophenol dissolved from off the filter in 100 c.c. of absolutely neutral alcohol. The alcohol solution of the tribromophenol is diluted with 100 c.c. of water and titrated with N/20 KOH solution, using phenolphthalein as indicator. The potassium hydroxide solution should be previously standardised against pure phenol. During this titration a slight yellow colour may appear in the solution. This should not, however, be sufficient to obscure the end point. If the yellow colour deepens in shade during the progress of the titration and is sufficient to mask the end point, the determination should be discarded and a new one run.

Where large quantities of organic matter are present the above methods cannot be used. In such cases Mumford (*Chem. News*, 1913, **107**, 253) recommends the determination of the phenol by sulphonating, nitrating and observing the colour. A suitable volume of the unknown is warmed with a few c.c. of concentrated sulphuric acid to 30–90° for one minute. A 10% solution of potassium nitrate is added in sufficient quantity to oxidise the organic matter and nitrate the phenol-sulphonic acid and the mixture warmed or boiled until pale yellow or colourless. The mixture is cooled, concentrated ammonium hydroxide added and the colour of the ammonium picrate produced compared with a standard of phenol-sulphonic acid treated the same way. The method is claimed to be sensitive to 0.0001 grm. phenol and sufficiently accurate for most purposes.

None of the above methods are applicable for the estimation of phenol in mixtures with cresols or other phenolic substances. For estimation in such mixtures see page 291.

A toxicological examination for phenol is not infrequently necessary, owing to the numerous instances in which poisoning has ensued from the accidental administration of the substance internally. In such cases the mouth and esophagus are commonly white, soft, and corroded, but are sometimes found hardened and shrivelled.

The stomach is usually white, contracted, thickened, and shrivelled, but is sometimes intensely congested, with destruction of the mucous membrane. Occasionally, no abnormal appearance is observable. The intestines are usually thickened and congested. The bladder is generally nearly empty; any urine present will have a dark colour.

In testing animal matters for phenol the odour is a most valuable indication. For the recognition of the poison the suspected matters are cut up and well shaken with water acidified with sulphuric acid. The liquid is then distilled as long as bromine water renders the distillate milky, and the tests for phenol applied to the distillate. The characters of most service are: the odour; the reactions with ferric chloride, sodium hypochlorite, and bromine; and the property of coagulating albumin.

The distillate obtained as above is concentrated by shaking with ether, separating the ethereal layer, and examining the residue of its evaporation; when the amount of phenol is very small, the ether should be shaken with a little dilute sodium hydroxide, the alkaline liquid concentrated, and exactly neutralised by dilute sulphuric acid before applying the foregoing tests.

In cases of suspected poisoning it must be remembered that phenols exist normally in minute quantity in urine, and are formed in small quantity during putrefaction.

CRESOLS

Methylhydroxybenzenes $C_6H_4(CH_3)(OH)$

Cresol is the next higher homologue of phenol. It is therefore phenol in which one of the nuclear hydrogens is replaced by methyl. As shown on page 288 it exists in three isomeric modifications: the ortho, meta and para. All three occur abundantly in coal tar. Whilst the proportions of the three vary considerably with different tars an average ratio in coke oven tar produced in the United States is about 5 parts phenol: 3 parts ortho-cresol: 4 parts meta-cresol: 3 parts para-cresol.

The principal source of the cresols is the crude tar acids obtained from coal tar, as described under phenol. In the fractional distillation of these crude acids, after the phenol fraction is off, there is obtained a crude ortho-cresol fraction followed by a meta-para-cresol fraction. On account of the closeness in b. p. of the meta and para no good separation of these two isomers is obtained by fractional distillation. The ortho-cresol fraction is further purified by partially crystallising and separating the crystals from the mother liquor. The meta- and para-cresols, if pure materials are desired, must be separated by chemical means. The commonly used procedures for this separation take advantage of differences in their sulphonic acids.

The cresols show physical and chemical properties as outlined in the following table:

	Ortho-cresol	Meta-cresol	Para-cresol
M. P.	30.6	11.0	36.0
B. P. °	191.4	202.3	201.8
Sp. gr. at 25°	1.0449	1.0335	1.0334
Solubility in water at 25°	1 in 50	1 in 50	1 in 60
Refractive index at 40°	1.53719	1.53322	1.53187
Highest bromo-derivative	Br_2; m. p. 52°	Br_3; m. p. 82°	Br_2; m. p. 49°
Highest nitro-derivative	$(NO_2)_2$	$(NO_2)_3$	$(NO_2)_2$

The three cresols are nearly similar to one another in toxicity and bactericidal action. They possess about half the toxicity of phenol and about twice the bactericidal value. They are much less corrosive to the skin than phenol.

The cresol specified by the United States Pharmacopœia is a mixture of the three isomers. It is described as follows:

"Cresol occurs as a colourless or yellowish to brown-yellow, highly refractive liquid, becoming darker or assuming a reddish tint with age and on exposure to light, and having a phenol-like, sometimes empyreumatic odour.

"One mil of Cresol dissolves in about 50 mils of water, usually forming a cloudy solution; it is miscible with alcohol, ether, benzene, petroleum benzine, or glycerin; it is dissolved by solutions of the fixed alkali hydroxides.

"Sp. gr.: 1.030 to 1.038 at 25°.

"Not less than 90% by volume of Cresol distils between 195° and 205°.

"A saturated aqueous solution of Cresol is neutral or slightly acid to litmus, and becomes blue-violet on the addition of ferric chloride T. S.

"A solution of 1 mil of Cresol in 60 mils of water is not more than slightly turbid (hydrocarbons)."

Qualitative Tests for Cresols.—As a rule the cresols respond to the general tests for phenols given on page 272. Distinction between the three when present in only small quantity is difficult.

According to Nördlinger, the 3 modifications of cresol may be distinguished by their behaviour with ammonia. When a few drops of orthocresol are shaken with a few c.c. of ammonia solution the mixture becomes bluish on standing—like a dilute solution of cupric sulphate—but after a few days it acquires a deep indigo-blue colour and becomes opaque. Paracresol, when treated similarly, gives a transparent pale yellow liquid. Metacresol also gives a transparent liquid, which at first has a faint steel-blue colour, afterward becoming bluish, but the tint is distinguishable from the deep indigo-blue yielded by orthocresol.

Denigès states that the three cresols give characteristic colours when treated in small quantity with 4 c.c. glacial acetic acid, 2–3 drops 40% formaldehyde and 1 c.c. sulphuric acid.

Estimation of Meta-cresol.—The method of Raschig (*Zeits. angew. Chem.*, 1900, 31, 795) gives a very satisfactory way of estimating meta-cresol in the presence of the ortho- and para- isomers.

The method is based upon the fact that upon nitration 1 grm. of metacresol yields almost exactly 1.74 grm. of trinitrocresol, whereas ortho- and paracresol are destroyed. 10 grm. of the cresol are weighed into a small Erlenmeyer flask, and 15 c.c. of sulphuric acid (66° Bé.) are added. The flask is heated for an hour in a steam oven. The contents are then poured into a flask of about a litre capacity, and cooled under the tap. 90 c.c. of nitric acid (40° Bé.) are poured into the small flask, shaken around, and then rapidly transferred to the large flask. The latter is then shaken round vigorously for about 20 seconds until solution is complete. After about a minute an energetic action commences, which lasts 5 minutes. After standing a further 5 minutes, the flask is emptied into a basin containing 40 c.c. of water, and is rinsed out with another 40 c.c. The trinitro-m-cresol, which separates out, is filtered off, dried at 95°–100°, and weighed. The results obtained are not affected by the presence of even large proportions of xylenols or ortho- and paracresol.

10% of phenol also does not effect the result, but if a larger proportion is present, some picric acid separates with the trinitrocresol.

Estimation of metacresol in mixtures of cresols according to H. Ditz (*Zeits. angew. Chem.*, 1900, **42**, 1050):

About 1 grm. of the anhydrous cresol mixture is weighed out, dissolved in water with the aid of some sodium hydroxide, and the solution diluted to 250 c.c. 2 portions of 25 c.c. each are transferred to well stoppered flasks, and decomposed with a sufficient quantity of Koppeschaar's bromide-bromate solution, and 10 c.c. of hydrochloric acid (1:1). After being shaken for exactly 1 minute, 20 c.c. of a 5% solution of potassium iodide are introduced, the iodine which separates titrated with standard thiosulphate after 1 hour, and the amount of bromine absorbed calculated from the result. The quantity of meta-cresol is then obtained from the equations

$$x + y = a \text{ and } \frac{3\ Br\ x + 2\ Br\ y}{108.08} = b,$$

in which x = the amount of metacresol; y, the sum of the ortho- and paracresol; a, the weight of the total cresols; and b the weight of bromine absorbed, hence:

$$x = a - y = a - \frac{2.2195\ a - b}{0.7397} = \frac{b - 1.4798\ a}{0.7397}$$

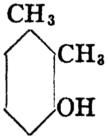
If a cresol mixture contain any traces of water, the latter is removed preferably by heating 5 to 10 grm. of the mixture in a small fractionating flask, and after removal of the water distilling over the cresol. The method assumes the cresols to be 100% pure. Impurities such as neutral oils interfere to a very marked degree. Any appreciable quantity of phenol or xylenols also interferes.

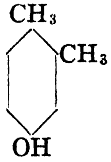
Analysis of mixtures of phenol and the cresols and of commercial cresylic acid is described on page 286.

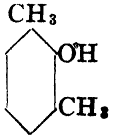
XYLENOLS

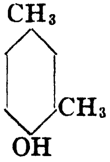
Dimethylhydroxybenzenes $C_6H_3(CH_3)_2(OH)$

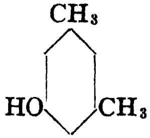
The xylenols are the next higher homologues of phenol. They can be regarded as xylenes in which one nuclear hydrogen is replaced by hydroxyl or as phenol in which two nuclear hydrogens are replaced by methyl. There are six isomeric xylenols, as follows:

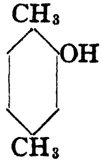

1–2,3
ortho 3


1–2,4
ortho 4


1–3,2
meta 2


1–3,4
meta 4


1–3,5
meta 5


1–4,2
para

They are obtained in the crude tar acids from coal tar in the fraction following the cresols. The individual members of the group are not commonly isolated.

The xylenols have the following boiling and melting points:

	M. P.	B. P.
1–2, 3	75.0	218 0
1–2, 4	62.0	225.0
1–3, 2	49.0	211.0
1–3, 4	26.0	211.5
1–3, 5	64.0	219.5
1–4, 2	74.5	211.5

A mixture of the xylenols is slightly less toxic and corrosive than the cresols but has a higher bactericidal value, *viz.*, about six times that of phenol.

COMMERCIAL CARBOLIC ACIDS

Cresylic Acid

The terms "carbolic acid" and "cresylic acid" are used commercially more or less indiscriminately to denote the various grades of mixtures of the phenols of all degrees of purity.

Pure crystallised phenol is generally brought into trade as Phenol, U.S.P., Carbolic Acid, Pure, or Carbolic Acid No. 1. Liquid Carbolic Acid or Carbolic Acid No. 4 is generally pure phenol which has been liquefied by the addition of 10% of water.

Cresylic Acid No. 5 is a mixture of the three cresols of a purity less than U.S.P. Cresol and containing generally more of the ortho-isomer.

Crude Cresylic Acid, 97–99% Straw Colour and Crude Carbolic Acid, 95% Dark, etc. are, as their names imply, mixtures of the phenols containing the specified amount of tar acids. They may or may not contain appreciable quantities of phenol, C_6H_5OH. Crude Carbolic Acid, 25%, etc. are coal tar oils containing the specified percentage of tar acids.

Determination of Tar Acid Content.—The evaluation of such crude products for their tar acid content is best arrived at by the following procedure as used by the Barrett Company: (Hill, *J. Ind. Eng. Chem.*, 1923, 15, 799).

A 100 c.c. sample of the oil at 25° is measured into a 200 c.c. distilling flask and distilled to decomposition, the distillate being collected in the tar-acid funnel (Fig. 18). The volume of the distillate is carefully read at 25° and, if no solids have separated, is extracted with three successive portions of 100 c.c. each of 10% sodium hydroxide solution. In each case after the soda is added to the oil, the whole is thoroughly shaken and is then allowed to settle completely before drawing off the soda layer. The volume of the residual oil after complete settling is carefully noted at 25°. The decrease from the volume of the distilled oil before extraction to the volume after extraction is the per cent by volume of phenols.

In the case of samples containing so much naphthalene as to show separated solids at 25°, the temperature of the three measurements may be raised to 40°, or even 60°, extraction being made also at the same temperature.

If the sample contains over 35% tar acids, the quantity taken for distillation should be cut to 50 c.c. or 25 c.c. so as to give not more than 35 c.c. of tar acids. Before distillation the material should be made up to 100 c.c. with clean, dry kerosene. The result obtained should be multiplied by 2 or 4.

Where the sample to be tested contains water it should be removed by catching the first c.c. of distillate in a small separatory funnel containing a little saturated salt solution, separating the water and adding the oil to the rest of the distillate in the tar-acid funnel.

If no diminution in volume takes place on extraction, a trace of tar acids may be detected by acidifying the soda drawn off and noting the odour.

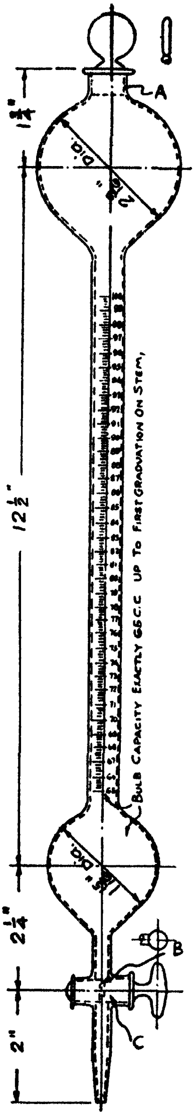


Fig. 18.—Separatory funnel for acid determination. A, Ground glass stopper; B, ⅜ in. drilled hole; C, ground glass stopcock.

An alternate method, in which the **tar acids** are liberated from their carbolate solution and measured directly, is the "liberation method" of the Barrett Company: (Weiss, *J. Ind. Eng. Chem.*, 1918, **10**, 911, Test H 12)—100 c.c. of dry oil at 25° shall be distilled to dryness. (Where the content of tar acids is very low, a distillation may be made on 200 c.c. so as to obtain a more accurate test.) If the acid content is over 35%, 50 or 25 c.c. of the sample should be taken. To insure complete distillation this should be diluted with kerosene before distillation. The distillate oil shall be shaken in a separatory funnel with successive 25 c.c. portions of 15–20% soda until no more tar acids are removed. The successive well-settled portions of carbolate shall be run into a separatory funnel and there washed with about 30 c.c. benzene. The washed carbolate shall be drawn off into a beaker. The benzene shall then be washed with about an equal volume of water and the washing added to the carbolate in the beaker. (If the benzene used in washing the carbolate is very darkly coloured the washing should be repeated.) The beaker containing the washed carbolate shall be heated on the steam bath until the odour of benzene is no longer noted. The benzene-free, washed carbolate shall then be cooled and acidified in a small beaker with 40% sulphuric acid, taking care to keep the mixture cool at all times. 65 c.c. of commercial xylene or solvent naphtha is measured into a "tar acid funnel" (see Fig. 18) at 25°. The liberated tar acids and sulphate solution are then poured through this layer of naphtha several times, drawing material off at the bottom of the funnel into the original beaker and pouring it back into the top of the funnel. This washes out the beaker and allows all the tar acids to be absorbed by the naphtha. The funnel shall then be allowed to stand until the layers separate perfectly clear, when the sulphate solution shall be drawn off and the increase in volume of the naphtha at 25° taken as the dry tar acids present. This method, when carefully run, gives results practically identical with the first method described.

The further analysis of carbolic acids of low tar acid content is described under Dip Oil (page 297).

Analysis of Carbolic Acids of Purity 95% or Better.—A good rough idea of the composition of the tar acids in a crude carbolic acid may be arrived at by determining the boiling range. The details of this test are exactly similar to that described for benzene on page 207, 4th Ed. or Vol. VI, this Ed., except that the asbestos pad supporting the flask should have a hole 1½ in. in diameter and the thermometer used should have a range of 170–230° and should be graduated in ⅕°. Specifications to insure uniformity of composition are generally based on this test, several points in the distillation range being specified. The actual percentages of the various phenols are seldom determined.

Acid Composition.—Where an actual quantitative determination of the separate phenols is desired it is carried out by thoroughly purifying the phenols, fractionating them and examining the fractions.

This method was suggested by J. M. Weiss and later developed by Weiss and Downs (*J. Ind. Eng. Chem.*, 1917, 9, 569).

Among further modifications which have been proposed may be mentioned those of Fox and Barker (*J. Soc. Chem. Ind.*, 1917, 36, 842) and Dawson and Mountford (*J. Chem. Soc.*, 1918, 113, 935).

The method suggested below makes use substantially of the purification as recommended by Weiss and Downs, the fractionation of Fox and Barker and the investigation of the fractions of Dawson and Mountford. The method is tedious and must be carried out with the utmost care to give good results.

300 to 350 grm. of the Crude Acid shall be taken in a separatory funnel and dissolved in 800 c.c. of 20% sodium hydroxide solution. If the Crude Acids are tarry it is advisable to distil them quantitatively before dissolving them in sodium hydroxide.

The carbolate in a separatory funnel shall be extracted five times successively with 100-c.c. portions of pure benzene. The manipulation shall be: add the benzene to the carbolate, mix thoroughly by shaking and allow to settle. Draw the carbolate into another separatory funnel and draw the benzene into a third separatory funnel. Repeat the agitation with fresh benzene four times mores, using the two original separatory funnels for this purpose. Finally, after running the washed carbolate into a beaker, rinse each of the funnels which contained carbolate, twice, with 25 c.c. each of water, and add the water to the carbolate in the beaker. Take the third separatory funnel, which contains the combined benzene, and wash twice with 50 c.c. of water, adding this water also to the carbolate in the beaker. Bring the carbolate in the beaker to a gentle boil until the odour of benzene disappears. No odour of creosote shall be evident in the carbolate at this point. If such odour appears, the washing has not been properly carried out and must be repeated. The carbolate purified of oil is ready for acidification after cooling. The benzene used for extraction may be discarded.

The purified carbolate shall be placed in a separatory funnel and acidified with sulphuric acid of 25% strength (sp. gr. 1.21 at 15.5°). The beaker containing the carbolate shall be rinsed with water and the rinsings added to the carbolate in the funnel. During acidification the mass *must* be kept *below* 40° by immersion in a bath of cold water. Test for acidity should be made from time to time with litmus paper. *More than a very slight excess* of acid (5 to 10 c.c.) must not be added after litmus shows a red colour. When acidification is complete, the funnel shall be allowed to stand until complete separation has taken place and the lower layer of sodium sulfate solution is perfectly clear or at most shows a slight opalescence. This settling requires from 3 to 4 hours. After settling is complete the sulphate layer shall be drawn off and kept for further treatment. The carefully separated acid layer shall be drawn down into a weighed 500 c.c. round-bottomed short ring neck flask and kept there until further treatment.

The sulphate solution shall be returned to the separatory funnel which contained the separated tar acids, which still has a thin film of tar acids adhering to the walls. The sulphate liquor shall be extracted three times with successive portions of 100 c.c. each of pure benzene and the benzene extracts combined in a separatory funnel of about 500 c.c. capacity. The benzene extract shall now be extracted with two successive portions of 25 c.c. each of 20% sodium hydroxide solution, or until the soda solution separates nearly colourless. The benzene can then be discarded. The sodium hydroxide solution shall then be warmed until all odour of benzene disappears and acidified with enough 25% sulphuric acid to make slightly acid. This shall be allowed to settle completely, the lower layer of sulphate drawn off and discarded, and the upper layer of acids added to the flask containing the main amount of the separated acid. This flask shall now be weighed and the weight of wet crude acids recorded.

The wet acids obtained are subjected to fractional distillation. The apparatus used consists of a round bottom flask connected with a Young's 8-pear column. An accurate thermometer, reading in 0.5° or less, is inserted at the top of the column. A suitable condenser is provided. The distillation is conducted at the rate of about one drop per second until a temperature of 170° is reached. The distillate up to this point is collected in a separatory funnel. Sufficient salt is added to it to saturate the water layer, causing any tar acids present to rise to the surface. These are carefully separated and put back in the distillation flask. This flask should be reweighed and the weight of the *dry* acids recorded.

The distillation is again started and continued at about one drop per second up to 210° (Distillate *A*). The first few drops containing water are collected separately, the acid separated and returned to *A*. This distillate *A* is weighed and mixed with exactly half its weight of *o*-cresol (m. p. 30.4 or above). It is refractionated in the same way cutting a first fraction (*B*) up to 195° and a second (*C*) up to 207°. These fractions should be received in tared flasks, which should be immediately tightly stoppered and weighed. Fraction *B* consists essentially of a mixture of the phenol and o-cresol, and fraction *C* of a mixture of the three cresols.

For the examination of fraction *B*, it is first carefully dried with a few lumps of fused calcium chloride. If its phenol content is high, as shown by a sp. gr. at 25° of 1.061 or more, its m. p. is determined directly. If the sp. gr. is below this figure a sufficient weighed quantity of pure phenol is added to a weighed quantity of the fraction to bring its sp. gr. above 1.061. The melting point is now carefully determined using an air jacketed 6 × 1 in. test-tube equipped with a stirrer and accurate thermometer with a range of about 0–50° and graduated in 0.2° or less. The mixture is stirred in the test-tube until crystallisation sets in and the temperature after reaching a maximum begins to fall again. The maximum is recorded as the m. p. and corresponds to a phenol content as shown in Table I.

The phenol content so obtained (m) may be calculated back to dry acids as follows:

a = weight of dry acids
b = weight of fraction B
c = weight of fraction C
d = weight of fraction B taken for test
e = weight of pure phenol mixed with weight d
h = weight of phenol in B = weight of phenol in dry acids
x = per cent phenol in dry acids

$$h = \frac{(d + e)m - 100c}{100} \cdot \frac{b}{d}$$

$$X = \frac{[(d + e)m - 100c]\,b}{ad} = \frac{100h}{a}$$

The weight $b - h$ may be assumed to be *o*-cresol.

Fraction *C* which is a mixture of the three cresols may be evaluated by a somewhat similar procedure.

The method depends on the fact that equal weights of *o*-cresol and *m*-cresol depress the freezing point of *p*-cresol to the same extent. In the application of the method a known weight of the unknown fraction *C* is mixed with a known quantity of pure *p*-cresol giving a mixture, the freezing point of which is determined. From this the % *p*-cresol in the mixture and hence in *C* and in the dry acids can be obtained from the freezing point curve corresponding with the figures given in Table II. The calculation is exactly similar to that given for phenol in the preceding paragraph.

Similarly, C is mixed with a known proportion of *o*-cresol giving a mixture, the freezing point of which is also determined. From this the % of *o*-cresol in the mixture and hence in C may be derived from the freezing points recorded in Table III. These temperatures correspond to a freezing point curve which lies between the curves representing the changes produced in the freezing point of *o*-cresol by the addition of *m*-cresol and *p*-cresol respectively. Again the calculation of *o*-cresol in C is similar to that for phenol. In this case, however, it must be remembered that *o*-cresol is also present in B and also that *o*-cresol was added to the dried acid. If k is the *weight* of *o*-cresol in C, the weight of *o*-cresol originally in the dried acids (of weight a) will be $k + b - h - \frac{a}{2}$

The % *m*-cresol in the dry acids will be obtained by difference, *i. e.*, 100 − % phenol − % *o*-cresol − % *p*-cresol.

The above method is fairly accurate for phenol but is somewhat rough for the cresols.

TABLE I

Weight % phenol	100	95	90	85	80	75	70
Freezing point	40.5°	37.9°	35.2°	32.4°	29 5°	26.5°	23.4°

TABLE II

p-cresol, %	100	95	90	85	80	75	70	65
Freezing point	34.15°	30.7°	27.2°	23.6°	20.0°	16.3°	12.3°	7.8°

TABLE III

o-cresol, %	100	95	90	85	80	75	70	65
Freezing point	30 45°	28.05°	25.6°	23.1°	20.4°	17.5°	14.4°	11.0°

Pyridine Bases.—The determination in crude carbolic acid of small quantities of pyridine bases is effected by steam distilling the bases from the solution of the acid in alkali and titrating the distillate. The method is approximate for the reason that all the bases are calculated as true pyridine. The following is the method as used by the General Bakelite Company:

100 c.c. of the sample is measured out into a 1,000 c.c. flask and 240 c.c. of distilled water added, followed by 260 c.c. of 1.2 sp. gr. sodium hydroxide solution made from pure sodium hydroxide. The flask is provided with a Kjeldahl connecting bulb to prevent any caustic from being carried over mechanically and connected with a water cooled condenser. The outlet of the condenser is provided

with an adapter which dips into a 500 c.c. Erlenmeyer flask containing 50 c.c. of N/5 hydrochloric acid and a few drops of Methyl Orange. All connections must be tight and the adapter must dip into the acid to avoid loss of pyridine. Approximately 200 c.c. is distilled over, the condenser and adapter rinsed into the Erlenmeyer flask with distilled water, and the excess acid titrated with N/5 sodium hydroxide. One c.c. of N/5 acid is equivalent to 0.01582 grm. pyridine. In the event that more than 0.7% pyridine is present, it is necessary to increase the quantity of absorbing acid and distillate or to decrease the quantity of cresol taken for the test.

Neutral Tar Oils.—A very fair comparative idea of the neutral oils present in a crude carbolic acid may be obtained by dissolving 10 c.c. of the acid in 40 c.c. of 10% sodium hydroxide solution in a stoppered 100 c.c. cylinder, diluting with 50 c.c. of water, shaking and letting it stand 10 minutes when the naphthalene or neutral oils will rise to the surface and their amount can be roughly estimated. This test is known as the "10:40:50 Soda Solubility."

A fair quantitative estimation is obtained by difference from the determination of tar acid content described on page (290).

Where a more accurate estimation of small quantities of neutral oils is desired the following procedure is used: 100 grm. of the acid to be tested is dissolved in 200 c.c. of 1.3 sp. gr. sodium hydroxide solution and diluted with 200 c.c. of water. The mixture is steam distilled until the distillate comes over clear, showing no more oil. The distillate is extracted in a separatory funnel with 200 c.c. ether in two successive 100 c.c. portions. The ether extracts are combined and washed successively with 15 c.c. 10% sodium hydroxide solution to remove any phenols, with 15 c.c. water, with two successive portions of 10 c.c. each of 20% sulphuric acid to remove pyridine bases, and finally twice more with 15 c.c. portions of distilled water. The extract is put into a weighed 200-c.c. flask and the ether slowly evaporated off, the last few drops being evaporated in the cold by blowing a gentle stream of air into the flask. The flask and contents are reweighed, the increase in weight in grm. representing the % neutral oils.

Hydrocarbon Number.—Where the acid consists almost wholly of cresols (and has therefore a definite molecular weight) a much simpler and at the same time more accurate method of arriving at the neutral tar oils is the determination of "Hydrocarbon Number," which is the number of c.c. of 10% sodium hydroxide solution which can be added to 10 grm. of the cresol without producing turbidity. The test, as carried out by the Barrett Company, consists of weighing out 10 grm. of the cresol into a small flask and titrating it with exactly 10% (by weight) sodium hydroxide solution, with constant shaking, until turbidity is reached. With a little practice the end point is very sharp. The calculation of Hydrocarbon Number to % neutral oils is generally omitted. The relation between the two is, however, shown by the following table:

Hydrocarbon No.	% Neutral Oils
16	3.4
18	2.9
20	2.4
22	1.9
24	1.45
26	1.0
28	0.7
30	0.45
32	0.33
34	0.25
36	0.20

Water.—The determination of water in crude carbolic acid is best carried out by distilling the acid with a neutral naphtha. 100 c.c. of the acid is mixed with an equal volume of solvent naphtha (commercial xylol) and distilled until the distillate comes over clear and free from water. The distillate is collected in a suitable graduated vessel and the volume of water separating to the bottom is read off. A very satisfactory apparatus for this determination is the familiar "Water in Tar Funnel."

DIP OILS AND COAL TAR FLOTATION OILS

The oil fractions from the distillation of coal tar which are heavier than water come into trade, with more or less refinement, as dip oils, flotation oils, creosote oils and crude carbolic acid.

The crude carbolic acids and dip oils are generally clean distillate oils of boiling range about 170–300° and containing a quantity of tar acids or phenols according to the specification under which they are sold. The commonest percentages are probably the 15% and 25% tar acid oils. These oils in combination with various other ingredients form the basis of a large number of insecticides and disinfectants, the value of which is dependent both on the tar acid content and on the neutral oil. So-called "First Quality" oils are sufficiently free from naphthalene and other solid hydrocarbons so that no separation takes place at temperatures as low as 0°. "Second Quality" oils have the naphthalene left in them and are therefore apt to separate considerable solids even at ordinary temperatures.

The coal tar flotation oils show a wide variation one from the other, some of them being very similar to the dip oils while others are much higher boiling or even tarry. For delicate flotation operations the uniformity of the tar acid content is thought to be highly important since the selective action of the oil in flotation of ores seems to be largely dependent on this component. For the flotation of the sulphide copper ores such oils are used in a proportion of about one pound of oil per ton of ore, the flotation cell being kept slightly acid. Conditions once adjusted for the particular oil are very easily upset by a variation such as in tar acid content, an excess of tar acids giving the effect of "overoiling" the ore.

The analysis of dip oils or flotation oils may involve determinations of boiling range, tar acid content, "limpid point," water, pyridine bases, specific gravity. Where dip oils are used for making emulsifiable disinfectants (see page 320) the colour of the oil is also often important as influencing the colour of the emulsion.

Tar Acids.—The estimation of tar acids in such oils has already been fully described on page 289.

Bulb Distillation.—The bulb distillation test for distillation range on these oils is exactly similar to that described for benzene (see Vol. VI) except that a 0–400° thermometer (see page 83) is used and an asbestos pad with a 2 in. hole.

Limpid Point.—This test is an indirect measure of the naphthalene or other solid hydrocarbons present. The limpid point is determined by warming the oil until all naphthalene is in solution and slowly cooling, stirring with a thermometer until crystals of naphthalene begin to separate. For low limpid point oils an ice and salt bath is necessary. As soon as crystals appear the oil is warmed with stirring at a rate of about 2° per minute, the limpid point being the point at which the crystals disappear. In determining limpid point the temperature is not commonly carried below $-20°$. If crystallisation does not begin at this temperature the oil is seeded with a minute crystal of naphthalene and if crystallisation is still not induced the oil is considered to be "limpid at $-20°$."

Where the oil is clean but so dark coloured as to obscure the limpid point, it is distilled to complete dryness, the limpid point being determined on the entire distillate. This can, of course, be done only when the oil can be distilled practically 100%, and the result is therefore not influenced.

Pyridine Bases.—This estimation is carried out on the extracted oil from the estimation of tar acids. The oil is extracted in the tar acid funnel with three portions of 100 c.c. each of 20° Bé. sulphuric acid. The same precautions called for in the tar acid determination must be observed here. The contraction in volume of the oil is the per cent pyridine bases.

Water.—The estimation of water is the same as is described for water in Crude Carbolic Acid on page 297.

Colour.—The colour of the oil may be conveniently compared with inorganic solutions as colour standards. The following is the set of colour standards used by the Barrett Company and the method of their application: the standards are made up from the following three basic solutions.

Solution A.—25 c.c. 33½% C. P. hydrochloric acid diluted to 1000 c.c. with distilled water.

Solution B.[1]—100 grm. $FeCl_3.6H_2O$ and 60 c.c. of A.

Solution C.—100 grm. $CoCl_2.6H_2O$ and 100 c.c. of A.

The formulæ of the individual standards are as follows:

Standard	Sol. A, c.c.	Sol. B, c.c.	Sol. C, c.c.	Distilled water, c.c.
C 1	250	2.0	1.5	
C 2	250	4.0	2.5	
C 3	250	8.0	4.0	
C 4		16.0	4.0	250
C 5		20.0	5.5	200
C 6		40.0	10.0	200
C 7		80.0	15.0	200
C 8		130.0	15.0	100
C 9		250.0	20.0	55
C 10		250.0	20.0	

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[1] This solution may also be conveniently prepared by dissolving 30 grm. C. P. Fe_2O_3 in 125 grm. 33½ % C. P. HCl and diluting to 160 grm.

The standards are preserved in one-ounce "French square" bottles. Comparison with the standards is made by filling a similar bottle with the oil and viewing by strong transmitted daylight. If the sample is darker than C 10, 1 c.c. of the oil is pipetted into 25 c.c. of benzol and the colour of the resultant solution compared with the standards. If the colour of the diluted oil is C 2 the colour of the original is said to be C 12 and so on, adding 10 to the standard in each case where the sample is so diluted. If the colour is darker than C 20, 1 c.c. of the diluted sample (1:25) is diluted with 25 c.c. of benzol and compared with the standards, the colour being reported as C 21, C 22, etc.

CREOSOTE OIL

While the term "creosote" originally referred to wood-tar products, these oils have been so widely replaced by coal tar oils for the purposes of "creosoting" or preserving timber that the present day creosote oil is almost exclusively coal tar oil. These oils are therefore considered here, whereas true "creosote" is discussed in a later section.

Creosote oils are used for impregnating or painting timber in order to prevent decay by inhibiting the growth in the wood of the decay producing fungi. Their action is both as an actual fungicide and insecticide and as a water-resistant filler for the wood.

Specifications for the better grades of creosote oil are drawn so as to insure a straight coal tar distillate. Adulteration with undistilled tar or with petroleum products is guarded against.

For the treatment of railroad ties an admixture containing usually about 20% of undistilled tar is widely used. Such an oil is known as "creosote-coal tar solution." Water gas-tar distillates and mixtures of such distillates with the undistilled tar are used to some extent for creosoting, although their fungicidal value is not considered equal to that of the coal tar-oils.

Typical specifications are those of the American Wood-Preservers' Association for the grade 1 distillate oil and coal tar solution and that of the British Engineering Standards Association.

A. W. P. A. Specification for No. 1 Creosote Oil

1. The oil shall be a distillate of coal-gas tar or coke-oven tar.[1] It shall comply with the following requirements:

2. It shall not contain more than 3% of water.

3. It shall not contain more than 0.5% of matter insoluble in benzol.

4. The sp. gr. of the oil at 38° C. compared with water at 15.5° shall be not less than 1.03.

5. The distillate, based on water-free oil, shall be within the following limits:

Up to 210°, not more than 5%.
Up to 235°, not more than 25%.

6. The residue above 355°, if it exceeds 5%, shall have a float-test of not more than 50 seconds at 70°.

7. The oil shall yield not more than 2% coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Approved, 1917; *adopted*, 1921; *amended and adopted*, 1923.

A. W. P. A. Specification for Creosote—Coal Tar Solution[2]

1. The oil shall be a coal-tar product of which at least 80% shall be a distillate of coal-gas tar or coke-oven tar, and the remainder shall be refined or filtered coal-gas tar or coke-oven tar. It shall comply with the following requirements:

2. It shall not contain more than 3% of water.

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[1] Owing to the complexity of the chemical composition and physical properties of coal-tar creosote oil, and to the fact that some of the same compounds and properties which characterize coal-tar creosote are found in certain petroleum derivatives, the determination of the purity of creosote oil is difficult. When there is not certain assurance that the oil is a pure product, the following tests will aid in arriving at an opinion as to its coal-tar origin:

A. Fraction distilling between 210° and 235° is usually solid or contains some solids when cooled to 25°.

B. All of the fractions up to 315° contain tar acids in varying amounts, usually at least 1%, calculated on the amount of the fraction tests. (See MANUAL—Creosote, Analysis, Tar Acids.)

C. The sp. gr. of the fraction 235° and 315° is usually not lower than 1.025 and sp. gr. of the fraction between 315° and 355° is usually not lower than 1.085 and 38° compared with water at 15.5°. However, some pure coal-tar distillates fall slightly below these limits.

If the oil does not comply with at least one of the foregoing tests it is undoubtedly not a pure coal-tar creosote.

Approved and adopted, 1923.

[2] This specification is submitted for the guidance of those desiring to use the coal-tar addition to creosote for ties only, which practice is firmly established and widely followed. The creosote-coal-tar solution is not recommended as equal to creosote in preservative quality, and should be used for ties only when the available supply of creosote is inadequate.

Approved, 1917; *adopted*, 1921.

3. It shall not contain more than 2% of matter insoluble in benzol.

4. The sp. gr. of the oil at 38° C. compared with water at 15.5° shall be not less than 1.05 or more than 1.12.

5. The distillate, based on water-free oil, shall be within the following limits:

Up to 210° not more than 5%.

Up to 235° not more than 25%.

6. The residue above 355°, if it exceeds 26%, shall have a float-test of not more than 50 seconds at 70°.

7. The oil shall yield not more than 6% coke residue.

8. The foregoing tests shall be made in accordance with the standard methods of the American Wood-Preservers' Association.

Approved, 1917; *amended*, 1918; *adopted*, 1921; *amended and adopted*, 1923.

B. E. S. A. Specification No. 144 for Creosote Oil

"The sp. gr. shall be not less than 1.015 and not more than 1.07 at 38° (100° F.) when compared with water at the same temperature. The material shall become completely liquid on being slowly warmed to 38° (100° F.) with stirring, and on cooling down shall remain completely liquid after standing for two hours at 32° (90° F.) The amount of water in the creosote shall not exceed 3%. When 100 c.c. measured at 38° (100° F.) of the dry creosote are distilled from a 250 c.c. distillation flask at such a rate that the distillation is complete in about 20 minutes, there shall distil at 760 mm. pressure:

up to 205° (401° F.) not more than 7 c.c.

up to 230° (446° F.) not more than 40 c.c.

up to 315° (599° F.) not more than 78 c.c.

the volumes of all fractions being measured at 38° (100° F.).

The residue above 315° (599° F.) shall be soft and not sticky and its weight shall be not less than 22 grm.

The amount of tar acids shall be not less than 5%, and not more than 16% by volume.

The amount of matter insoluble in benzol (benzene) shall not exceed 0.4% by weight.

METHODS OF ANALYSIS

The methods of testing creosote oil given below are those generally accepted in the United States.

Water.—The apparatus consists of a copper still 6 in. by 3½ in., provided with a ring burner to fit the still, a connecting tube, trough condenser and graduated separatory funnel ("water-in-tar funnel"). The apparatus is assembled as shown in Fig. 19.

200 c.c. of oil is measured in a graduated cylinder, and poured into the copper still, allowing the cylinder to drain into the still for several minutes. The lid and clamp are attached using a paper gasket slightly wet with oil around the flange of the still. Heat is applied by means of the ring burner, which is placed just above the level of the oil in the still at the beginning of the test, and gradually lowered when most of the water has distilled over. The distillation is continued until the vapor temperature, indicated by the thermometer with the bulb opposite the offtake of the connecting tube, reaches 205°. The distillate is collected in the separatory funnel. When the distillation is completed, and a clear separation of water and oil in the funnel has taken place, the water is read by volume and drawn off; any light oil distilled over with the water is returned to the oil in the still after it has cooled sufficiently. The dehydrated oil from the still shall be used for the distillation and other tests.

Retort Distillation.—The retort shall be a tubulated glass retort of the form and approximate dimensions shown in Fig. 20 with a capacity of 250 to 290 c.c. The capacity shall be measured by placing the retort with the bottom of the bulb and the end of the offtake in the same horizontal plane, and pouring water into the bulb through the tubulature until it overflows the offtake. The amount remaining in the bulb shall be considered its capacity.

The condenser tube shall be a suitable form of tapered glass tubing of the following dimensions:

Diameter of small end	12.5 mm.;	permissible variation 1.5 mm.
Diameter of large end	28.5 mm.;	permissible variation 3.0 mm.
Length	360.0 mm.;	permissible variation 4.0 mm.

An asbestos shield of the form and approximate dimensions shown in Fig. 3 shall be used to protect the retort from air currents and to prevent radiation. This may be covered with galvanised iron, as such an arrangement is more convenient and more permanent.

The thermometer shall conform to the following requirements:[1] the thermometer shall be made of thermometric glass of a quality equivalent to suitable grades Jena or Corning make. It shall be thoroughly annealed. It shall be filled above the mercury with inert gas which will not act chemically on or contaminate the mercury. The pressure of the gas shall be sufficient to prevent separation of the mercury column at all temperatures of the scale. There shall be a reservoir above the final graduation large enough so that the pressure will not become excessive at the highest temperature. The thermometer shall be finished at the top with a small glass ring or button suitable for attaching a tag. Each thermometer shall have for identification the maker's name, a serial number and the letters "A. S. T. M. distillation."

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[1] A.S.T.M. D38–17D

The thermometer shall be graduated from 0 to 400° at intervals of 1°. Every fifth graduation shall be longer than the intermediate ones, and every tenth graduation beginning at zero shall be numbered. The graduation marks and numbers shall be clear-cut and distinct.

The thermometer shall conform to the following dimensions:

Total length, maximum	385.0 mm.	
Diameter of stem	7.0 mm.;	permissible variation 0.5 mm.
Diameter of bulb, minimum	5.0 mm.;	and shall not exceed diameter of stem.
Length of bulb	12.5 mm.;	permissible variation 2.5 mm.
Distance, 0° to bottom of bulb	30.0 mm.;	permissible variation 5.0 mm.
Distance, 0 to 400°	295.0 mm.;	permissible variation 10.0 mm.

The accuracy of the thermometer when delivered to the purchaser shall be such that when tested at full immersion the maximum error shall not exceed the following:

From 0 to 200°	0.5°
From 200 to 300°	1.0°
From 300 to 375°	1.5°

The sensitiveness of the thermometer shall be such that when cooled to a temperature of 74° below the boiling point of water at the barometric pressure at the time of test and plunged into free flow of steam, the meniscus shall pass the point 10° below the boiling point of water in not more than six seconds.

The retort shall be supported on a tripod or rings over two sheets of 20-mesh gauze, 6 in. square, as shown in Fig. 20. It shall be connected to the condenser tube by a tight cork in the tubulature with the bottom of the bulb 0.5 in. from the surface of the oil in the retort. The exact location of the thermometer bulb shall be determined by placing a vertical rule graduated in divisions not exceeding 1/16 in. back of the retort when the latter is in position for the test, and sighting the level of the liquid and the point for the bottom of the thermometer bulb. The distance from the bulb of the thermometer to the outlet end of the condenser tube shall be not more than 24 nor less than 20 in. The burner shall be protected from draughts by a suitable shield or chimney.

Exactly 100 grm. of oil shall be weighed into the retort, the apparatus assembled and heat applied. The distillation shall be conducted at the rate of at least one drop and not more than two drops per second, and the distillate collected in weighed receivers. The condenser tube shall be warmed whenever necessary to prevent accumulation of solid distillates. Fractions shall be collected at the following points: 210, 235, 270, 315 and 355°. The receivers shall be changed as the mercury of the thermometer passes the dividing temperature for each fraction. When the temperature reaches 355°, the flame shall be removed from the retort, and any oil which has condensed in the off-take shall be drained in the 355° fraction.

The residue shall remain in the retort with the cork and the thermometer in position until no vapours are visible; it shall then be weighed. If the residue is to be further tested it shall then be poured directly into the brass collar used in the float test or into a tin box and covered and allowed to cool to air temperature. Care must be taken not to pour at a temperature high enough to cause loss of oil vapours. If the residue becomes so cool that it cannot be poured readily from the retort, it shall be re-heated and completely melted by holding the bulb of the retort in hot water or steam, and not by application of flame.

For weighing the receivers and fractions, a balance accurate to at least 0.05 grm. shall be used.

During the progress of the distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer.

When any measurable amount of water is present in the distillate it shall be separated as nearly as possible and reported separately, all results being calculated on a basis of dry oil. When more than 2% of water is present, water-free oil shall be obtained by separately distilling a larger quantity of oil, returning to the oil any oil carried over with the water, and using dried oil for the final distillation.

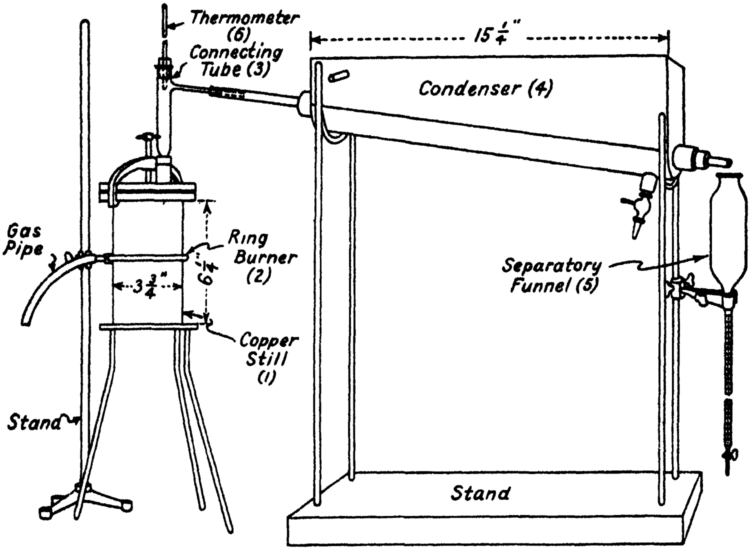


FIG. 19.

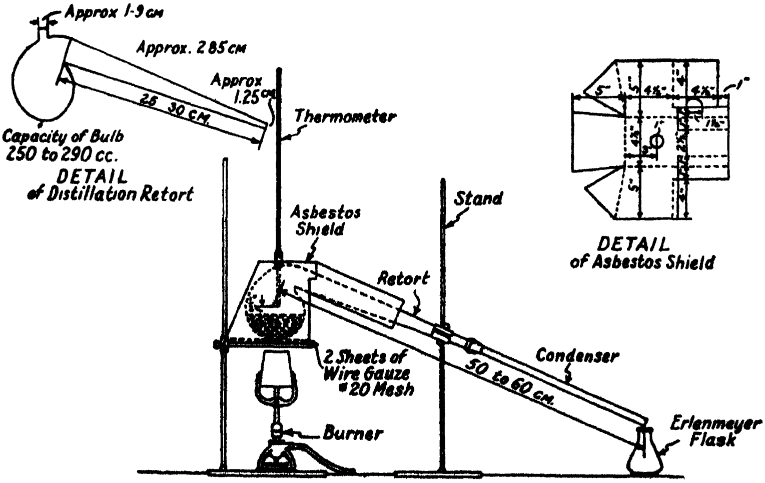
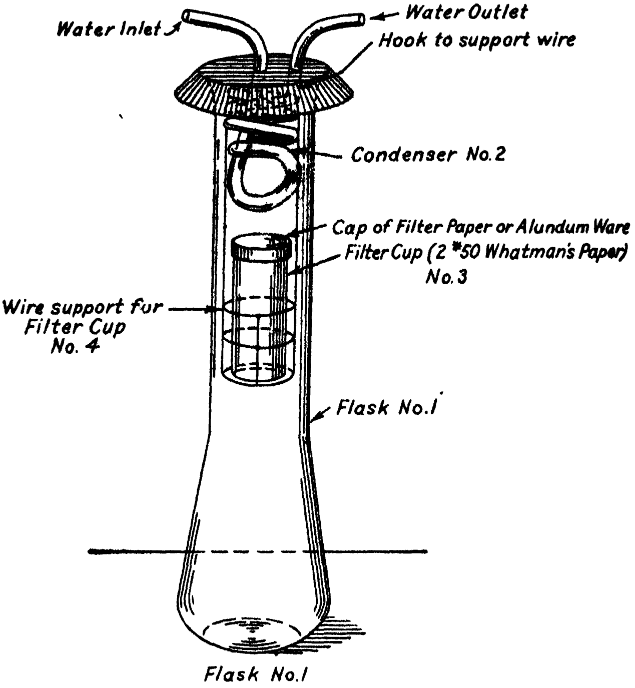


FIG. 20.—Assembly of distillation test for heavy oil. A. S. T. M. D-38-17.

Float Test on Residue above 355°.—The float apparatus shall consist of an aluminium float with brass collars as shown in detail in Fig. 22. In addition to the dimension and weight specifications, it is required that when loaded with 5.5 grm., the height of the rim of float above the water shall be 8.5 mm. ± 1.5 mm.



Extractor For Free Carbon

FIG. 21.

The thermometer shall be of 0–80° range graduated in 0.2°. The water bath shall be cylindrical and at least twice the diameter of the float. The minimum depth of water shall be equal to the diameter of the bath.

The residue above 355° from the retort distillation test shall be completely melted at the lowest possible temperature and mixed thoroughly until homogenous and free from air bubbles.

The brass collar shall be placed with the smaller end on a brass plate which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chloride or nitrate and

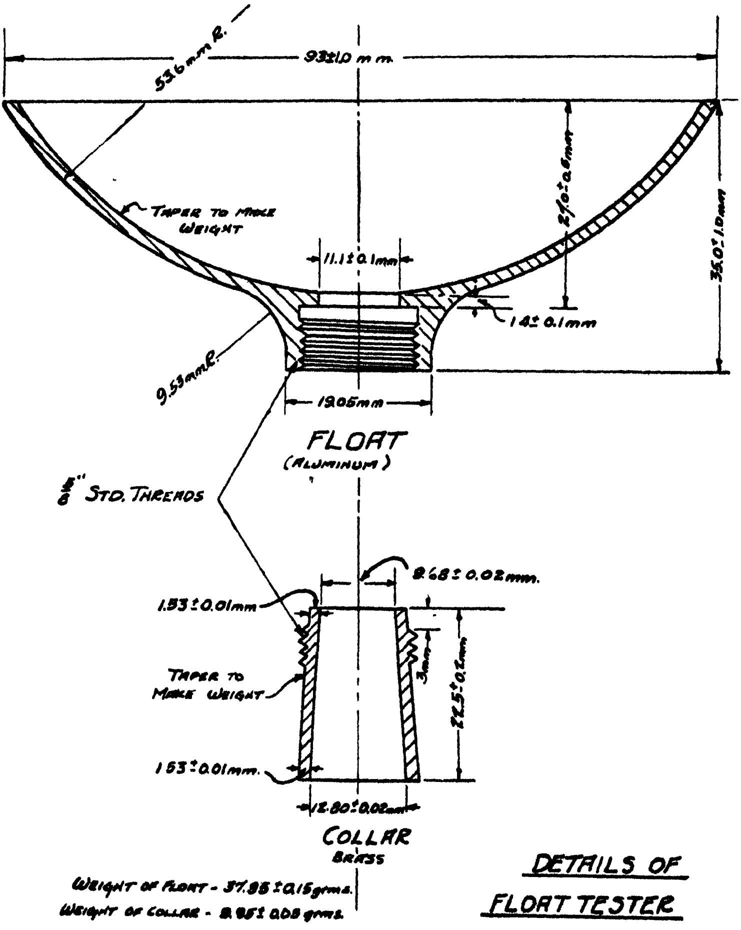


FIG. 22.

then with mercury. The sample shall be poured into the collar in any convenient way until slightly more than level with the top. It shall be cooled to room temperature, placed in water maintained at 5° for 5 minutes, after which the surplus material shall be removed by means of a spatula, or steel knife, which has been slightly heated. The collar and plate shall then be placed in a tin cup containing ice water maintained at 5° ± 1°, and left in this bath for at least 15 minutes.

The water bath shall be filled with water and the thermometer inserted with the top of its bulb approximately one inch below the surface of the water and one inch from the side of the bath. The water shall be heated to the temperature at which the test is to be made. This temperature shall be accurately maintained and shall at no time throughout the test be allowed to vary more than 0.5° from the temperature specified.

After the material to be tested has been kept in the ice water for not less than 15 minutes nor more than 30 minutes, the collar with its contents shall be removed from the plate and screwed into the aluminum float and immersed in water at 5° for one minute. Any water shall then be removed from the inside of the float and the latter immediately floated in the warm bath at the temperature specified. As the plug of material becomes warm and fluid, it is forced upward and out of the collar until the water gains entrance into the saucer and causes it to sink.

The time in seconds between placing the apparatus on the water and *when the water breaks through the material* shall be determined by means of a stop watch, and shall be taken as a measure of the consistency of the material under examination. An average of three such tests shall be reported.

Special precaution should be taken to insure the collar fitting tightly into the float and to see that there is no seepage of water between the collar and float during the test.

Small differences in the shape or dimensions of the apparatus may make great differences in the results obtained. Therefore, the laboratory should be sure that the apparatus closely conforms to the specification.

Coke Residue.—The determination shall be made in a platinum (or Rhotanium or Palau) crucible of 20 c.c. to 30 c.c. capacity with close fitting cover, heated by a Bunsen or Tirrell burner.

The test shall be made on the residue above 355° from the retort distillation. The residue shall be thoroughly mixed and 1 grm. weighed into the tared crucible.

The cover shall be applied and the crucible placed on a platinum, nichrome or fire clay triangle over the burner, with the bottom of the crucible 6 to 8 cm. from the top of the burner. The burner flame shall be regulated to a height of 20 cm. when burning free, and the crucible shall be exposed to the full flame for 7 minutes. At the end of this period, the flame shall be removed, the crucible transferred to a dessicator and allowed to cool, after which it shall be weighed. The residue in the crucible after ignition is "fixed carbon" *i. e.*, coke. The test shall be carried out in a part of the laboratory free from draughts.

The percentage of coke thus obtained shall be figured back to the original sample of oil. For instance the retort distillation gave 29% residue to 355°. The residue contained 28% fixed carbon.

Then

$$\frac{29 \times 28}{100} = 8.1\% \text{ Coke in oil}$$

Benzene Insolubles (Free Carbon).—The apparatus consists of the extraction apparatus known as the "Underwriters' extraction flask." Extraction thimbles,[1] caps of filter paper or alundum (30 mm. inside diameter by 14 mm. high), carbon filter tubes of 37 mm. size are used.

Dried oil from the water test shall be passed hot through a 30 mesh sieve to remove foreign substances. 10 grm. or more of the filtered oil shall be weighed into a 100 c.c. beaker and digested with pure toluene at 90°–100° for a period of *not over thirty minutes.* The solution shall be stirred to insure complete digestion. A carefully dried extraction thimble shall be weighed in a weighing bottle and placed in a filter tube supported over a breaker or flask. The thimble shall be wet with toluene and the toluene-oil mixture decanted through the filter. The beaker shall be washed with toluene until clean, using the camel's-hair brush as a "policeman" to detach solid particles adhering to the beaker. All washings shall be passed through the filter cup. The filter cup shall then be given a washing with pure benzene and allowed to drain. The cap shall be then placed on the cup and the whole placed in the extraction apparatus and extracted with pure benzene until the descending benzene is completely colourless. The cup shall then be removed, the cap taken off and the cup dried at 97°–100°. After drying it shall be allowed to cool in a dessicator and weighed in the weighing bottle. The increase in weight represents matter insoluble in benzene.

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[1] These can be made of Whatman number 50 filter paper. To make a cup, two 15 cm. circles shall be taken and one cut down to a diameter of 14 cm. A round stick about one inch in diameter shall be used as a form. The stick shall be placed in the center of the circles of filter paper, the smaller inside and the papers folded symmetrically around the stick to form a cup about 2½ inches long. A little practice enables the operator to make these evenly and quickly. After being made they shall be soaked in benzol to remove grease due to handling, drained, dried in a steam oven at 97°–100°, cooled in a dessicator and kept there until used.

If the first filtrate shows evidence of insoluble matter, it should be refiltered. The 30 minute-time allowed for digestion must not be exceeded.

Tar Acids if called for may be determined by either of the methods described on page 289.

CRESYLIC ACID DISINFECTANTS AND DIPS

Cresylic acid or creosote disinfectants and dips are on the market under distinctive trade names in great numbers. They fall into three main divisions, as follows:

1. Emulsifying dips or disinfectants which form a milky emulsion with water.
2. Soluble dips or disinfectants which mix with water in practically all proportions to form a clear solution.
3. Disinfectant powders, the base of which is generally an inorganic earth impregnated with cresylic acid or a dip made from it.

Phenol Coefficient.—All of these products are generally sold on the basis of their bactericidal value or "phenol coefficient." This coefficient is the ratio of the minimum effective dilution of the article which will kill *B. typhosus* in a specified time under certain fixed conditions to the minimum dilution of phenol which will accomplish the same result. There are two principal methods for its determination: the Rideal-Walker (R. W.) method (Am. Jour. Pub. Health **3**, 575) which is almost exclusively used in England and to a considerable extent in the United States, and the Hygienic Laboratory (H. L.) method (U. S. Pub. Health Report, 1921, **36**, 1559. which is preferred in the United States. The methods differ in the strength of the broth used, the details of the technique and the interpretation of the results. The H. L. method gives results about 20% lower than the R. W. method. The details of the two methods are given below.

RIDEAL-WALKER PHENOL COEFFICIENT TEST

Materials

Nutrient Broth.

Liebig's extract of meat	20 grm.
Peptone (Witte's)	20 grm.
Salt (sodium chloride, C. P.)	10 grm.
Distilled water	1 litre

Boil the mixture for 30 minutes, then filter, and neutralize with normal sodium hydroxide solution, using phenolphthalein as indicator. In order to avoid contaminating the broth with phenolphthalein it is advisable to take an aliquot part of the filtered broth—say 10 c.c.—and titrate this with N/10 sodium hydroxide, calculating the amount of normal sodium hydroxide necessary for the neutralisation of the remainder of the broth. Add, when quite neutral, 15 c.c. of normal hydroxide acid. This will give the broth a reaction of +1.5%. The broth is then made up to the litre, filtered and sterilised. Where two or three litres are prepared at one time, as is customary, the broth is distributed in 500 c.c. flasks on the following day and again sterilised. Five c.c. are then run with the aid of a small separating funnel into sterile test tubes, which, after plugging with sterile cotton wool are placed in the steam steriliser for half an hour or so.

Standard Carbolic Acid.—As carbolic acid crystals are very often contaminated by cresols to such an extent as to make them unreliable for purposes of bactericidal control, their purity should be established by a determination of the solidifying point (point of constant temperature) on at least 50 c.c. of the material with the thermometer in the liquid. The point is very sharp, the thermometer showing a constant temperature for a period of from 5 to 10 minutes. The solidifying point of the crystals is 40.5 but anything over 40.0 may be accepted. A 5 per cent. (by weight) stock solution is then prepared and standardised by titration with decinormal bromine. From this solution (which keeps indefinitely in stoppered bottles) the various working strengths are made up by diluting some comparatively large quantity, such as 100 c.c. to the desired volume; this serves to eliminate the error introduced by measuring out small quantities of strong acid.

Dilutions of the Disinfectant.—A stock solution or emulsion should be prepared in 100 c.c. stoppered cylinder, with sterilised distilled water—10% if the coefficient be under 1, and 1% if over 1. Ten c.c. of this stock solution are used in preparing each of the 4 dilutions required for the test. Thus, working with a sample having a coefficient under 1, if it is desired to prepare a dilution of 1:70, 10 c.c. of the 10% stock solution are diluted with 60 c.c. of distilled water, and in the case of a preparation having a coefficient over 1, where the dilution required is 1:700, 10 c.c. of the 1% stock solution should be diluted with 60 c.c. of water. In preparing dilutions of the unknown, the limitations of the test must not be overlooked. The following is a safe rule for general work, expressing the dilutions as multiples of the carbolic acid dilution:

With coefficients of 1 and under .	X	0.1
With coefficients above 1 but not exceeding 10........	X	0.5
With coefficients above 10 but not exceeding 20.......	X	1.0

For example, assuming that the strength of the carbolic acid control be 1:100 when it is desired to test a sample having a coefficient of 10, the dilutions to be recommended would be 1:950, 1:1000, 1:1050, 1:1100.

The Broth Culture.—*B. typhosus*, grown in R. W. broth and incubated for 24 hours at 37° provides the test culture. To insure even distribution of the bacilli in the broth culture, and to avoid the necessity of filtration, the culture tube should be shaken and allowed to rest for half an hour before it is finally removed from the incubator, the temperature of which should not vary more than half a degree from day to day. It is advisable to make a sub-culture every 24 hours from the previous 24-hour culture, even if on many days no test is to be performed but as this tends to attenuate the organism it should be continued for not more than one month, after which a fresh sub-culture in broth should be taken from a month-old agar culture. By this means a culture not varying much from day to day in resistance to disinfectants is obtained, making the selection of the proper dilution of carbolic acid much easier than it would be if the culture from which the 24-hour growth is obtained were older on one occasion than on another

Apparatus.—A special test tube rack is used. It contains two tiers, the upper having holes for 30 test tubes, in two rows, each row containing three sets of five; this tier is for the sterilised broth tubes, each of which is numbered with grease pencil. The lower tier is for the medication tubes—four with disinfectant dilutions and one with the carbolic acid control dilution, the latter being placed in the fifth hole. The lower tier is provided with a copper water bath to keep the temperature of medication within the prescribed limit—15° to 18°. The test tubes being numbered in rotation it will be seen that the first medication tube is used for inoculating broth tubes, 1, 6, 11, 16, 21 and 26, the second for 2, 7, 12, 17, 22 and 27, etc.

The inoculating needle used should be composed of thin aluminium rod, with a short piece of platinum wire (26 U. S. gauge) passed through and twisted round an eye in the end of the rod, or otherwise firmly fixed thereto. The wire is made into a loop at the end and bent slightly in the center to allow of a fair sized drop being taken up for each inoculation. Satisfactory results cannot be expected when one tube is inoculated with a full drop and a mere film is introduced into another. The length of the wire to end of loop should be about 1¾ inches. After a little practice it is easy to obtain a satisfactory drop by dipping the needle in the medicated culture and bringing it out with a slight jerk. The loop used has an internal diameter of 3 mm.

The test tubes should be of fairly strong glass so as to minimise as far as possible the risk of breakage, and lipped, to facilitate manipulation of plugs. Five inches by ⅝ inch is the size recommended for use. The cotton wool plugs for both medication tubes and broth tubes should be well made, so that they can be withdrawn and replaced without loss of time. A convenient method is to place a thin flat piece of cotton wool over the mouth of the test tube, with a smaller piece in the center to form a core, and to push both into position with the aid of a thin glass rod.

A dropping pipette is used for the broth culture and is standardised to deliver 0.1 c.c. per drop. It is loosely plugged at the top with cotton wool, and when not in actual use is kept in a sterile test tube plugged at the mouth with cotton wool. For greater convenience the tube should be passed through the centre of the plug and fastened thereto with wire.

In addition to the above, one or two each of the following are required: 1, 5 and 10 c.c. pipettes; 100 and 250 c.c. stoppered cylinders (with inverted beakers, to safeguard against dust after removal from steriliser); wire baskets to receive tubes for incubation or sterilisation. All pipettes and cylinders should be standardized.

Technique.—Before commencing the test it is necessary to ascertain the carbolic acid control dilution which will give the desired result—*i. e*., life in 2½ and 5 minutes. This is done by running a trial test with 5 dilutions of the carbolic acid only—say, 1:80, 1:90, 1:100, 1:110 and 1:120. 5 c.c of the control solution so ascertained are then pipetted into the fifth medication tube, the other 4 receiving 5 c.c. of the various dilutions of the disinfectant under test. To save time and apparatus, one pipette can be made to do service at this stage by starting with the phenol solution and following on with the highest or lowest dilution of the disinfectant, according as the coefficient is below or above one, rinsing out the pipette in each case with the next dilution before measuring off the sample for test.

The plug of the culture tube is now replaced by the culture pipette which, as explained above, has a plug attached to it with wire, at such a height that when the plug fits easily into the mouth of the culture tube, the point of the pipette is half way down the broth, and clear of the clumps. The first of the five medication tubes is now inocculated with five drops of the culture—*i. e*., 0.5 c.c. At intervals of half a minute each of the other medication tubes is inoculated in turn. By the time the fifth tube has been inoculated the organism in the first will have been exposed to the action of the disinfectant for two minutes, and after the next half minute a loopful of the latter is inoculated into the first broth tube, loopfuls from the other medication tubes being in turn inoculated into their respective broth tubes at the rate of one every thirty seconds. By the time the fifth broth tube has been inoculated from the fifth medication tube, the disinfectant in the first medication tube will have acted on the test organism for 4½ minutes, and after the next thirty seconds a loopful is introduced into broth tube 6, and so on. The actual test, therefore, occupies 17 minutes, and provides for six 2½-minute periods of contact in each of the five medication tubes.

It is open to the worker, of course, to adopt any convenient method of manipulating the tubes and plugs. The following procedure is given for the guidance of the inexperienced. The first medication tube is taken from the rack and the contents gently agitated for a second to insure even distribution of the bacilli; the plug having been taken out and grasped by the left little finger, the tube is held between the back of the left forefinger and front of the second. The corresponding broth tube (No. 1) is taken up by the right hand and transferred to the left between the thumb and forefinger, the plug being extracted and held by the little finger of the right hand. The tubes now being in position for inoculation, the needle, which should have been sterilised before the tubes were touched, is introduced into the medication tube, from which a loopful is taken and inoculated into the broth tube. The needle is sterilised in the flame (placed to the right) and pushed with a movement of the thumb well up between the first and second fingers of the right hand; the plugs are then replaced, the medication tube going back to the rack while the broth tube is subjected to a gentle agitation and placed in a wire basket on the right of the rack. This basket containing the thirty inoculation tubes and test form giving particulars of the dilutions, etc., is now placed in the incubator where it is allowed to remain for 48 hours at blood heat, when the results are read off. A moment's consideration of the manner in which the test has been conducted will suffice to indicate where the results of each sub-culture should be placed in the table.

The details given below of a test of disinfectant X show the form in which the results are set out; incidentally it shows the degree of refinement to which the test can be carried with a little practice and care.

The strength or efficiency of the disinfectant under test is expressed in multiples of carbolic acid, and is obtained by dividing the dilution of the disinfectant showing life in 2½ and 5 minutes by the carbolic acid dilution, which, of course, must show the same result. In the present instance this "figure of merit," or Rideal-Walker coefficient, is 20.0.

To avoid annoyance and loss of time caused by aerial contamination of tubes, etc., it is advisable to conduct the test in a room free from draughts; a further safeguard is provided by spraying or swabbing the floors and benches with an efficient disinfectant solution. Needless to add, all pipettes, etc., must be rigorously sterilized before use.

APPROVED TECHNIQUE OF RIDEAL-WALKER TEST

B. typhosus, 24 hours' broth culture @ 37°

Temperature of medication 15° to 18°

Sample	Dilutions	Time culture exposed to action of disinfectant, minutes						Sub-cultures	
		2½	5	7½	10	12½	15	Period of incubation	Temperature
Disinfectant X	1:1900	x						48 hr.	37° C.
Disinfectant X	1:2000	x	x					48 hr.	37° C.
Disinfectant X	1:2100	x	x	x				48 hr.	37° C.
Disinfectant X	1:2200	x	x	x	x			48 hr.	37° C.
Carbolic acid	1: 100	x	x					48 hr.	37° C.

$$\therefore \text{Rideal-Walker coefficient} = \frac{2000}{100} = 20.0$$

HYGIENIC LABORATORY PHENOL COEFFICIENT TEST

The test culture is a culture of *Bacillus typhosus*, Hopkins strain. Between periods of testing it is maintained on nutrient agar stabs, transferred at monthly intervals.

For at least 5 days before the test the culture is transferred at 24-hour intervals to successive tubes of the meat extract broth described below and incubated at 37°. Transfers are made with one standard loopful. The culture is filtered through sterile filter paper just before using. The test is performed with a 24-hour culture.

The phenol must comply with the requirements of the Eighth United States Pharmacopœia. Particularly the congealing point must not be below 40°. The crystals are kept in tightly stoppered amber-colored bottles in a dark and relatively cool place.

A 5 per cent original solution is made by adding 1 part by weight of phenol, liquefied by warming the bottle, to 19 parts of distilled water. A fresh solution is made for each day's use.

The Culture Medium.—Make meat extract medium as follows:

Beef extract (Liebig's)	3 grm.
Peptone (Armour's for disinfectant testing)	10 grm.
Sodium chloride	5 grm.
Water, distilled	1,000 c.c.

Boil for 15 minutes.
Make up to original weight by addition of water.
Filter through paper.
Tube, 10 c.c. to each tube.
Sterilise.
The pH value of this medium should be between 6.0 and 7.0.

Apparatus.—Glassware for measuring must be accurately graduated. It must be clean, dry, and sterile at the time of use. There will be needed—

1 c.c. capacity pipettes.
5 c.c. capacity pipettes.
1 c.c. delivery pipettes, graduated in tenths.
5 c.c. delivery pipettes.
100 c.c. measuring cylinders, graduated in 1 c.c., glass stoppered.
Seeding tubes, 1 x 3 inches, flared tops, round bottoms.

Racks consisting of blocks of wood with rows of holes for both the seeding tubes (before they are placed in the water bath) and the subculture tubes.

Wire loops must be carefully made and kept from damage. They are made as follows: a close cylindrical spiral is made by winding a piece of platinum wire, No. 23, B. & S. gauge, as tightly as possible about a piece of steel or other hard wire having a diameter of 0.072 inch (No. 13, B. & S. gauge) to complete a little more than four full turns. The long end of the wire is then bent sharply at right angles to the wound portion and parallel to the steel wire. The core is removed and the short end of the wire is clipped off so as to leave exactly four full turns to the coil. The successive turns of the spiral must touch one another continuously. The long end of the wire is attached to an aluminium handle.

A convenient support is provided on which to rest the loops so that a batwing Bunsen burner may be placed under each one successively.

A constant temperature bath is provided, capable of maintaining the seeding tubes at 20° during the time of the test. A well-insulated bath of large volume relative to the surface exposed is sufficient without thermo-regulating appliances.

Disinfectant Testing Machine.—The use of a disinfectant testing machine is optional. One is described in Reprint No. 462 from the U. S. Public Health Reports. A few modifications have proved useful. For example, the use of platinum instead of nichrome loops, and the practice of sterilising the subculture tubes covered with padded inverted troughs in the racks.

Dilutions of phenol and of disinfectants are made from the original liquid on the day of the test. For the dilutions of the disinfectant, a 5 per cent solution is made by adding 5 c.c. of the disinfectant to 95 c.c. of sterile distilled water. A standardised 5 c.c. capacity pipette is used for this purpose. After filling the pipette, all excess of the disinfectant on the outside of the pipette is wiped off with sterile gauze. The contents of the pipette are then delivered into a cylinder containing 95 c.c. of sterile distilled water and the pipette is washed out as clean as possible by aspiration and blowing out the contents into the cylinder. The contents of the cylinder are then thoroughly shaken and the dilutions up to 1:500 are made from it, using delivery pipettes for measuring. For those disinfectants which do not readily form a 5% solution, make a 1% solution, and from this make the dilutions greater than 1:100 in accordance with the second table of dilutions. If greater dilutions than 1:500 are to be made, a 1% solution is made from the 5% solution and the higher dilutions are made from this.

For the higher dilutions, delivery pipettes may be used. The following scale is used for making dilutions:

For dilutions up to 1:70, increase or decrease by a difference of 5 (*i.e.*, 5 parts of water); from 1:70 to 1:160, by a difference of 10; from 1:160 to 1:200, by a difference of 20; from 1:200 to 1:400, by a difference of 25; from 1:400 to 1:900, by a difference of 50; from 1:900 to 1:1800, by a difference of 100; from 1:1800 to 1:3200, by a difference of 200; and so on if higher dilutions are necessary.

It is important that the cylinders used for making the dilutions be correctly graduated. It is preferable to use standardised cylinders and pipettes.

Method.—This description applies to the hand method. For the use of the machine, follow the procedure of Reprint No. 462 from the U. S. Public Health Reports.

The object is to add 0.1 c.c. of typhoid culture to 5 c.c. of successive dilutions of the disinfectant and of phenol, and, after this addition, to transfer a loopful of each mixture to a separate subculture tube at periods of 5, 7½, 10, 12½, and 15 minutes. The subculture tubes are then incubated for 48 hours at 37°, and readings of growth or no growth are made and recorded.

Dilutions are made to cover the expected range of the disinfectant, and 5 c.c. of each dilution is placed in a seeding tube. Dilutions of phenol are made as follows: 1:80, 1:90, 1:100, 1:110, 1:120, and 1:130, and 5 c.c. of each is placed in a seeding tube.

The seeding tubes are placed in the water bath at 20° and a few minutes are allowed for their contents to reach this temperature.

To each seeding tube 0.1 c.c. of culture is then added seriatim, allowing 15 seconds for each addition. If there are 10 tubes of disinfectant dilutions, this will occupy 2½ minutes. At the end of 5 minutes from the time of adding the disinfectant to the first seeding tube, a loopful of the mixture is transferred from this tube to a subculture tube, and this is done from each successive seeding tube at 15-second intervals. This procedure is repeated after the lapse of 7½, 10, 12½, and 15 minutes from the time of the first addition of culture to the seeding tube. Each loop is placed on the support and flamed with the Bunsen burner immediately after use, and the use of several loops permits them to cool before they are needed again. The operator is therefore obliged to make a transfer every 15 seconds for 10 minutes.

The culture is best added to the seeding tube by holding the latter in a slanting position and touching the tip of the 1 c.c. pipette to the wetted surface exposed on its upper side. One-tenth c.c. is run in at the proper time and thorough admixture is assured by gentle shaking.

The dilutions of phenol are next treated in the same manner as those of the disinfectant.

The tubes are properly labeled and are placed in the incubator for 48 hours, at the end of which time readings of growth or no growth are made and entered in a table as + or − signs, respectively.

In the nature of the test it is unavoidable that discrepancies in the even oblique slant of the plus signs across the chart will occasionally be encountered;

but if these are numerous, a faulty technique is indicated and the test should be discarded. The same applies to accidentally contaminated tubes.

Determination of Coefficient.—The coefficient is the arithmetic mean of the sum of three ratios, expressed decimally. These ratios are, the denominator of the highest dilution of the disinfectant in whose subculture tube no growth occurs, divided by the corresponding figure for phenol, for the 5, 10, and 15 minute intervals, respectively.

Example

Sample	Dilution	Time of exposure in minutes				
		5	7½	10	12½	15
Disinfectant........	1:700	−	−	−	−	−
	1:800	+	−	−	−	−
	1:900	+	+	−	−	−
	1:1,000	+	+	+	+	−
	1:1,100	+	+	+	+	+
Phenol.......... ..	1:80	−	−	−	−	−
	1:90	+	−	−	−	−
	1:100	+	+	+	+	−
	1:110	+	+	+	+	−
	1:120	+	+	+	+	+
	1:130	+	+	+	+	+

$$\text{Coefficient} = \frac{\frac{700}{80} + \frac{900}{90} + \frac{1000}{110}}{3} = \frac{8.7 + 10.0 + 9.0}{3} = 9.2$$

EMULSIFYING DISINFECTANTS

These products are combinations of a tar acid oil, such as dip oil or creosote oil, with a soap of rosin or of a fatty acid. Besides the phenol coefficient, a complete analysis is sometimes necessary. The following methods, which are applicable to such materials, are taken from Bulletin 107, Bureau of Animal Industry, U. S. Dep. Agr.

Estimation ot Water.—50 grm. of dip is weighed into a 100 c.c. fractionating flask with a moderately high side tube, beyond the exit of which the neck should continue for not more than 1 in., and the flask is connected with a small water-cooled condenser and carefully heated with a smoky flame until oils come over freely and carry no trace of water with them, but the distillation should not be unnecessarily continued. The distillate is received in a properly graduated 25 c.c. cylinder, allowed some time to separate completely, and the volume of water read. The number of cubic centithe end-points of methyl-orange and phenolphthalein by 0.79. The only difficulty in the method is the determination of the point of neutrality toward methyl-orange, but a proper use of the standard of comparison will satisfactorily overcome this.

Recent work has indicated that the colouring-matters which tend to interfere with the accurate observation of the end-point with methyl-orange may be almost entirely removed from the solution by the use of animal charcoal. Powdered animal charcoal is digested on the steam-bath with dilute hydrochloric acid in sufficient quantity to decompose and dissolve all carbonates and phosphates present, then washed with hot water until the wash-water is free from chlorides, and finally dried and powdered.

In the course of an analysis, after the flask containing the acid extract from the dip has been heated upon the steam-bath until ether has been completely expelled, 1 to 1.5 grm. of the purified animal charcoal are added, and the flask, frequently shaken, is left upon the steam-bath for 30 to 60 minutes. The contents are then filtered, washed, and titrated as usual. After proper treatment with animal charcoal in this manner the solution will be a pale green in colour, possessing none of the muddy yellow tint which tends to obscure the end-point with methyl-orange.

Experiments have thus far failed to show that any inaccuracy is introduced into the method by the use of animal charcoal in the manner described.

Phenols.—50 grm. of dip are weighed into a 500 c.c. round-bottomed flask, 20 c.c. of 1:3 H_2SO_4 are added, and the phenols are distilled off with steam. The flask will require no heating if a rapid current of steam is passed into it, but may with advantage be packed in cotton or felt. Obviously the apparatus must be so set up and the distillation so conducted that particles of rosin may not be mechanically carried over by the current of steam. Toward the end of the distillation any naphthalene in the condenser is melted out by shutting off the water for a few minutes, or if separated earlier in sufficient quantity to threaten stoppage of the condenser tube, distillation is interrupted while hot water is run through the condenser. The distillate is received in a litre flask approximately marked for each 100 c.c. capacity and joined to the condenser by a cork which is pierced by a small glass tube connected to a small U-tube containing a little dilute sodium hydroxide. The latter acts as a trap to prevent any loss of the distilled phenols. Distillation is continued until 1 or 2 c.c. collected in a test-tube give no reaction with any appropriate reagent for phenols, such as ferric chloride. A volume of 800 c.c. is ample in nearly all cases.

A supply of benzene should be prepared by shaking a good grade of benzene with dilute sulphuric acid, then with dilute sodium hydroxide 2 or 3 times, and then passing through a dry filter. A small wash-bottle containing some of this benzene will be found very useful for rinsing the necks of separatory funnels, etc. Of this purified benzene 150 c.c. are measured out conveniently at hand, the contents of the U-tube and 5 c.c. of 1:1 H_2SO_4 are added to the distillate, and the latter is shaken up and poured into a separatory funnel of 1,500 c.c. capacity, the flask being rinsed out with successive portions of the 150 c.c. benzene. When all is in the funnel 25 grm. of clean sodium chloride are added for each 100 c.c. of distillate, and the funnel is well shaken for 5 minutes and left at rest ½ hour. The aqueous layer is then run off slowly and completely, the funnel being allowed to stand until there is no further separation. The benzene solution of phenols and hydrocarbons is transferred to a 500 c.c. Erlenmeyer flask, whilst the aqueous portion is poured back into the separating funnel and extracted twice more in the same way, 100 c.c. of benzene being used each time. The funnel should always be gently handled after the aqueous portion has been drawn off, to prevent any impurities from the sodium chloride which have deposited upon its sides from becoming mixed with the benzene solution. The 3 benzene extracts are united in the Erlenmeyer flask, 15 c.c. of pure sodium hydroxide solution, 1:2, is added, and the contents of the flask are subjected to a rotatory motion for some time in order that the phenols may be taken up by the sodium hydroxide as completely as possible.

After the addition of a few grains of sand the flask is immersed in a water-bath, connected with a condenser, and all but 40 to 50 c.c. of the benzene distilled off. With the aid of a wash-bottle containing water and provided with a fine jet, only a small portion of water being used at a time, the contents of the flask are next carefully washed into a 150 c.c. separatory funnel. With proper manipulation the flask should be completely washed when the volume of aqueous portion in the separatory funnel amounts to not more than 50 c.c. 10 c.c. of strong sulphuric acid (100 c.c. pure concentrated H_2SO_4 to 120 c.c. water) are next slowly introduced with gentle rotation of the funnel, the addition of acid being interrupted and the funnel cooled whenever it becomes unpleasantly warm to the hand. 2 or 3 drops of methyl-orange are now added; and if on mixing the contents of the funnel the lower layer does not acquire a pink colour, the addition of acid is continued until acidity is assured. Sufficient benzene is then added to make the 2 layers in the funnel approximately equal in volume, the funnel is thoroughly shaken and, with loosened stopper, left at rest for 2 hours. After that time the aqueous layer is slowly and completely run out, the analyst making sure that on longer standing no more will drain down from the sides of the funnel. The benzene solution of phenols is then ready to be transferred to the measuring tube.

The measuring tube consists of a glass-stoppered pear-shaped bulb of about 100 c.c. capacity, joined at its tapering end to a tube about 1 foot long and of a capacity of 25 to 30 c.c. This tube is accurately graduated to contain 25 c.c. at 20° in divisions of 1/10 c.c. (see Fig. 23).

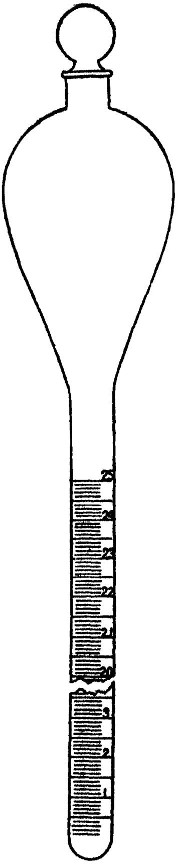

FIG. 23.[1]

The apparatus is cleaned thoroughly with soap powder and hot water, and dried, best spontaneously, though alcohol and ether may be used if pure. Perfect cleanliness is essential to insure a properly shaped meniscus. Between 15 and 16 c.c. of sodium hydroxide solution, 1:3, is brought into the tube with a pipette. The sodium hydroxide should not be allowed to come in contact with the interior of the bulb or the upper part of the tube. After a few moments about 1 c.c. of benzene is added, and after waiting a little the height to the top of the now almost flat meniscus is noted. The benzene solution of phenols is next transferred from the separatory funnel to the tube, care being used to avoid mixing with the soda; the separatory funnel is washed out with a little benzene which is also transferred to the tube, and the height of the meniscus is again noted. This latter may often be obtained more accurately at this point. The tube is then stoppered, vigorously shaken for 3 minutes, and set aside for at least 3 hours. An occasional rapid rotation of the tube between the palms of the hands will insure a complete separation of the layers. Each c.c. increase in volume of the sodium hydroxide solution may be taken to represent 1 grm. of phenols. All readings of the tube should be taken at the top of the meniscus and at a temperature as near 20° as practicable.

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[1] The use of this cut was kindly granted by the Bureau of Animal Industry, U. S. Dept. of Agriculture.

This method of treating the distilled phenols is essentially that of Spalteholz (*Chem. Zeit.*, 1898, **22**, 58–59), though the details of its execution were not imparted in the original communication and had to be worked out independently.

From certain experiments it seems possible that a continuous extraction apparatus[1] may be successfully employed to extract phenols from the aqueous distillate of the dip, using benzene as the solvent, and introducing sodium hydroxide solution into the distillation flask of the apparatus at the beginning of the operation to retain the extracted phenols. When the extraction is completed the small flask of the apparatus will contain all the phenols, dissolved in a limited amount of sodium hydroxide solution and overlaid by about 50 c.c. of benzene. The contents of the flask may then be brought readily and completely into a separatory funnel and acidified in the usual manner. Certain exigencies of the work in this laboratory[2] have rendered somewhat inconvenient at the present time a practical test of this method of procedure in the routine examination of dips submitted for analysis.

Determination of Rosin Acids.—Resins in general have been shown to contain at least 3 different classes of bodies (Allen, Vol. 4): (1) resin acids or anhydrides, (2) esters of these or similar acids, (3) indifferent neutral substances, perhaps hydrocarbons. Common rosin, or colophony, contains, between 83.4 and 93.8% of free rosin acids or anhydrides. The remaining 6 to 17% consists of neutral substances, soluble in ether and not extracted from ethereal solution by aqueous sodium hydroxide, and accordingly there would seem to be no practicable means of distinguishing and separating them from the coal-tar hydrocarbons of the dip. Apparently, then, the analyst must be content with a determination of the amount of rosin acids present, which will represent about $9/10$ of the amount of rosin actually used in manufacturing the dip. Either a gravimetric or a volumetric method may be employed.

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[1] Forms of extraction apparatus may be obtained of all ground-glass connections for extracting aqueous liquid, with solvents lighter than water and solvents heavier than water, or in the usual way as a Soxhlet extractor depending upon the use of special attachments for the several purposes intended. (Amer. Ed.)

[2] Bureau of Animal Industry, U. S. Dept. of Agric.

Owing to the degree of uncertainty attached to the exact combining equivalent of the rosin acids in each particular dip, the gravimetric method has an indubitable advantage in point of accuracy when properly carried out. But, as a matter of fact, the combining equivalents of a considerable number of rosin acids obtained from different dips in the gravimetric way in the course of analysis have been found to vary very little, not enough in any case to cause a possible error of 0.5% in the analysis of a dip of ordinary constitution. Moreover, in view of the difficulty of completely separating hydrocarbons from rosin acids, as is necessary in the gravimetric method, it is probable that the ordinary analyst without considerable practice in this particular operation will obtain quite as accurate results by the volumetric method as by the gravimetric. Accordingly the volumetric method would seem to recommend itself for use in ordinary routine work on account of its greater rapidity, simplicity, and probable equal accuracy under ordinary conditions, whilst the gravimetric method may be reserved for dips extremely high in rosin or for a confirmatory method in special cases.

For the estimation of rosin acids by either method it is most advantageous to make use of the residue left in the distillation flask after the estimation of phenols. From this residue all phenols and a large part of the hydrocarbons have been removed, hence the necessary extraction by ether is expedited. After cooling, the aqueous portion of the contents of the flask is poured into a separatory funnel, with as little rosin as possible, and extracted with ether. The aqueous portion is run off and discarded, the residue in the flask is completely dissolved and brought into the funnel with ether, 40 to 50 c.c. of water is added, and the funnel well shaken. The presence of insoluble carbonaceous matter will usually cause a persistent emulsion at the junction of the 2 layers, which may, in fact, entirely fill the lower part of the funnel.

This is wholly run off into a 300 c.c. Erlenmeyer flask and the ethereal solution well shaken again with successive portions of water, the water being run off each time to the clear ethereal solution, until the carbonaceous matter is wholly removed and separation takes place in the funnel quickly and cleanly. These wash-waters are all received in the flask containing the first separated emulsion, and this is heated upon the steam-bath until ether is expelled. The contents are then brought more or less completely upon a wet filter and washed with hot water. At this point the methods diverge.

Gravimetric Method.—In case the gravimetric method is to be employed, after a brief washing of the insoluble carbonaceous residue with hot water, both flask and filter are well drained. Both are then washed, first with a little absolute alcohol to remove water, then thoroughly with ether until all rosin is dissolved and the filtrate comes through colourless.

The united ethereal solution of hydrocarbons and rosin is now thoroughly shaken with about 40 c.c. of 15% sodium hydroxide solution. On separation there will be three layers. The lowest one usually contains very little rosin soap, and consequently holds but a small amount of hydrocarbons. It is best run off and washed separately with ether. One washing will usually free it completely from hydrocarbons.

After the first layer has been thus removed, about 50 c.c. of water is added to the funnel and the latter is well shaken. The lower layer of rosin soap is run off and followed by 5 to 10 c.c. of water without shaking, the funnel being given only a gentle rotatory motion. The remaining ether solution of hydrocarbons is washed twice with 20 to 25 c.c. of about 4% sodium hydroxide solution, each washing being followed by a little water as before described. These 2 washings with dilute sodium hydroxide are kept apart and not added to the main solution of rosin soap.

The main solution of rosin soap is now washed in a separatory funnel with successive portions of ether, followed through each time by 5 c.c. of water, as at first, until the ether is left nearly colourless. The ether extracts are shaken through in their order with the 2 washings of dilute sodium hydroxide already used, and a third if needed, each being followed with a few c.c. of water.

All the aqueous extracts are united in a porcelain dish or casserole, which should be not more than half-filled by them, and are evaporated on the steam-bath until ether is dissipated and the volume reduced to a convenient amount. The contents of the dish are then transferred to a separatory funnel with the aid of a spatula and hot water; strong sulphuric acid is added to decompose all rosin soap, and after complete cooling the rosin acids are extracted by ether and washed with water till free from sulphuric acid. The ethereal solution is brought into a weighed Erlenmeyer flask with a few grains of sand, the ether is distilled off, and the flask is heated in an oven at 110° until the absence of frothing on rotation shows elimination of water, it is then cooled and weighed.

Volumetric Method.—As alreay noted, the volumetric method proceeds identically with the gravimetric to the point where carbonaceous matter is brought upon the filter and washed with hot water. The washing in this case must be continued until the wash-water comes through entirely free from acid reaction. The main ethereal solution has meanwhile been brought into a flask and the ether distilled off. The filter funnel is set in the neck of this flask, and the carbonaceous matter is washed with hot alcohol previously rendered neutral to phenolphthalein, until free from rosin. The alcoholic solution of rosin is brought into a graduated flask, and an aliquot part, usually ¼, taken for titration with N/2 sodium hydroxide. The titration is conveniently carried out in a 200 c.c. Erlenmeyer flask in a volume of 100 to 125 c.c., the portion taken being diluted with neutralised alcohol to that amount.

Owing to the very dark colour of the liquid an external indicator is necessary. For this purpose alkali blue is best adapted. A few drops of a strong alcoholic stock solution are added to 25 or 30 c.c. of alcohol, which is then carefully neutralised with N/10 sodium hydroxide. Enough alkali blue should be added to produce a deep colour, almost a cherry red with no trace of violet when neutralised. This dilute indicator should be freshly prepared. A supply of small test-tubes 8 to 10 mm. in diameter and 60 to 80 mm. long should be at hand, cleaned and dried. When a test of the progress of the titration is to be made about 12 c.c. of prepared indicator is poured into 1 of these test-tubes, and to this is added a drop of the liquid under titration. If a violet colour appears, the solution still contains free rosin acid, and more N/2

NaOH must be added and the solution again tested with a fresh tube of indicator. If the indicator does not show a violet colour upon the addition of 1 drop of the liquid under titration, addition of the latter is continued drop by drop until an amount has been added approximately equal in volume to the amount of indicator originally in the tube, *i. e.*, ½ c.c. The continued absence of a violet colour after the addition of this amount indicates that the solution is either neutral or alkaline. The end of the titration then is reached when a greenish or violet tint just fails to appear. A fresh tube of indicator must be used for each test. It is best to proceed by running in 12 to 15 c.c. of N/2 sodium hydroxide at once, testing and continuing addition if necessary, a c.c. at a time, until the indicator shows alkalinity, then titrating back with N/2 hydrochloric acid, using perhaps 0.4 c.c. at a time until acidity is shown, and now working carefully with N/2 sodium hydroxide to exact neutrality. 1 c.c. of N/2 sodium hydroxide is considered to be equivalent to 0.162 grm. of rosin acids.

Phenolphthaelin may also be used as an indicator in a similar way, by preparing an alcoholic solution of quite a deep rose tint. The end-point of the titration will then be reached when the indicator, used in the same way as alkali blue, is no longer bleached by the addition of the liquid under titration. The colour change is not so marked as in the case of alkali blue, and consequently the end-point is not so sharp, though almost equally good results may be obtained with a little care and practice.

All the alcoholic solutions should be kept from contact with air as far as possible to prevent absorption of carbon dioxide.

CRESYLIC ACID DIPS

(Soluble Disinfectants)

Cresylic acid or cresol dips approximate in composition more or less closely the "liquor cresolis compositus" of the United States Pharmacopœia, 9th revision, 1916, being made from a linseed oil soap and cresylic acid comparatively free from hydrocarbons. A properly prepared dip of this character should, upon dilution in 100 parts of distilled water, yield a practically water-clear solution, showing absence of any notable amount of hydrocarbons or unsaponified oil. On dilution, however, with hard water there will naturally be some turbidity, caused by the precipitation of soap. A portion of the dip when treated with successive small portions of water should show itself miscible in all proportions. At no stage should there be any notable turbidity or separation of heavy oily globules of cresylic acid due to absence of sufficient soap.

The methods of analysis adopted are essentially the same as for coal-tar creosote dips, modified in details to suit the somewhat different composition of the substances.

Estimation of Water.—The distillate must always be received in a stoppered cylinder and treated with benzene and sodium chloride solution as described. The results will be about 0.5% too low. The addition of toluene or a similar hydrocarbon to the dip before distillation might possibly improve the results.

Estimation of Potash (or Soda) and Pyridine.—A preliminary test is necessary here to determine whether potash or soda is the alkali present. The test may be conveniently made by shaking about 10 grm. of dip with ether and a little dilute hydrochloric acid, drawing off the aqueous layer, and applying the flame test with a platinum wire, supplementing this with any other confirmatory test necessary or desirable. If potash is found to be the alkali present the factor 0.471 must be used in place of the factor 0.31 employed in the case of soda.

Estimation of Phenols.—Since the percentage of phenols will here be much higher than in coal-tar creosote dips, a smaller amount of dip must be taken for analysis, usually 15 to 20 grm. The amount should be as large as possible, in order that the greatest quantity of phenols within the capacity of the tube may be brought to measurement. A new opportunity for error is here afforded. Linseed oil possesses a low Reichert-Meissl number, 00 to 1.43 (See Vol. 2, page 483). This means that a small amount of volatile fatty acid will accompany the phenols through the stages of the process and tend to cause too high results. To determine the possible amount of this error 25 grm. of linseed oil was saponified, then acidified, and distilled with steam until 800 c.c. had been collected. The distillate was treated by the regular method and an increase in volume between 0.02 and 0.07 c.c. observed. In view of the fact that this quantity of soap is 4 or 5 times as much as would be present in an ordinary analysis, the error which is likely to arise from this source would appear negligible.

Estimation of Rosin or Fatty Acids.—The odour of the dip itself, and more especially the character of the residue left in the flask after the distillation of phenols, will inform the analyst whether rosin or fatty acids are to be estimated. Rosin will collect in a solid, hard button at the bottom, whilst fatty acids will form a liquid oily layer floating upon the surface of the aqueous contents. In either case the whole is extracted with ether, washed with water, and, after evaporation of ether, dissolved in neutralised alcohol and titrated with N/2 sodium hydroxide. 1 c.c. of N/2 soda will represent 0.138 grm. fatty acid anhydrides (Lewkowitsch, Chemical Technology and Analysis of Oils, Fats, and Waxes, 3d ed., Vol. 1, p. 639, 640) and 0.015344 grm. glycerin. Cresol dips containing rosin soap are not at present permitted in official dipping in the U. S. A.

Such a detailed analysis of a cresol dip would appear, however, seldom necessary. Phenols must of course be determined as accurately as possible. An examination of the odour and appearance of the residue left in the flask after distillation of phenols will indicate the character of the soap employed. If, then, the behaviour of the dip upon dilution is satisfactory and indicates the presence of sufficient soap, the only remaining question is whether there may be an unnecessary and possibly harmful amount of alkali present. In the presence of the large amount of cresylic acid contained in these dips there can be, strictly speaking, no "free alkali." The ideal cresol dip will, however, unquestionably contain no alkali above that necessary to obtain complete saponification of the linseed oil. An excess of alkali can be of no possible benefit and might conceivably be undesirable for several reasons. A useful test for the presence of an excess of alkali is that of Kernofer (*Schweiz. Wochenschrift Chem. Pharm.*, 1908, **46**, 19–20).

10 grm. of dip are thoroughly shaken in a small separatory funnel with 30 c.c. of a saturated solution of NaCl. After complete separation has taken place the lower aqueous layer is removed, diluted with an equal volume of water, and a few drops of phenolphthalein added. If the dip has been made from a perfectly neutral linseed-oil soap, there will appear at most but a slight reddening of the solution, which vanishes upon the addition of a drop of N/2 acid. If more acid is required to remove the pink colour, the presence of an excess of alkali is indicated. The test cannot be made quantitative, for experiments have shown that only a part of the excess of alkali actually

present is accounted for in this way, the remainder probably being thrown up in the form of alkali cresylate into the upper layer with the soap. It would seem, then, reasonable to demand that no dip treated as described should require more than a very few tenths of a c.c. of N/2 acid to remove the pink colour imparted by phenolphthalein to the sodium chloride extract.

DISINFECTING POWDERS

Disinfecting powders are of little importance at present, having been almost completely supplanted in use by the liquid disinfectants. They depend for their value on their content of phenols. The inorganic absorbent may be kieselguhr, clay, talc, lime, calcium sulphate, etc.

Good carbolic acid powders contain at least from 12 to 18% of crude carbolic acid, but higher strengths are obtainable. As much as 50% is absorbed by kieselguhr. All carbolic powders are liable to lose 1 or 2% by volatilisation. Some powders in the market contain but 5 or 6% of total oils, of which less than half is really carbolic and cresylic acids, the remainder being neutral tar oils.

For the estimation of the phenols and tar oils in disinfecting powders having a siliceous base, and in others containing the phenol in the free state, 50 grm. should be exhausted with ether in a Soxhlet-tube or similar arrangement. The ethereal solution is then agitated with about 20 c.c. of a 20% solution of sodium hydroxide, more or less than this quantity being employed according to the percentage of phenols supposed to be present in the powder (and about 1 c.c. of the reagent being used for every 1% of phenols in the sample). The ethereal layer is separated, and the alkaline liquid again shaken with ether, which is separated as before, and added to the main quantity. The united ethereal solutions are shaken with some sodium hydroxide solution, to dissolve out any phenols which may have escaped the previous treatment. The ether is then driven off by a gentle heat and the residual oils are weighed. The united alkaline liquid is boiled down in a flask to a small bulk (10 c.c.), and transferred to a burette or other suitably graduated tube, where it is treated with diluted sulphuric acid (1:3) in quantity sufficient after agitation to render the liquid distinctly acid to litmus. When the liquid has stood for some time and is *thoroughly cold*, the layer of separated phenols is measured. Each c.c. weighs about 1.050

grm., so that an addition of 5% to the volume gives the correct weight. The results are fairly accurate, but generally below the truth, owing chiefly to the solubility of phenols. Hence the liberation of the phenol should be effected in a liquid as concentrated as possible.

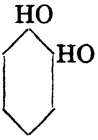
In cases in which the characters of the separated phenols suggest the presence of fatty acids, resin, or other foreign matter, the contents of the burette should be transferred back to the flask, diluted with water, and distilled. The phenols readily pass into the distillate, whereas any fatty or resin acids will remain in the retort.

In the case of powders made with lime, or others in which the phenols exist in combination, the method of direct extraction with ether or other solvent does not give accurate results. For the determination of the crude carbolic acid in such powders, the disinfectant value of which is very doubtful, the following method may be employed: 50 grm. of the sample should be mixed in a large mortar with 5 c.c. of water. Strong sulphuric acid, previously diluted with an equal volume of water, is then added very gradually, a few drops only at a time. After each addition the whole is well mixed together with a pestle. The addition of the acid, which should extend over some hours to avoid sensible rise of temperature, is continued until a minute fragment of the well-mixed contents of the mortar shows an acid reaction when placed on a piece of litmus-paper and moistened with water. If the mixture be pasty, sufficient sand is added to cause it to granulate, and the mortar is then covered up and left for some hours. By this method the lime, sulphuric acid, and water form hydrated calcium sulphate and the phenols are liberated. The product is then exhausted with ether in a Soxhlet-tube or similar contrivance.

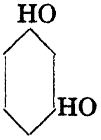
Whether isolated by the extraction or the distillation process, the crude carbolic acid obtained should be further examined for ***neutral tar oils***, which not infrequently constitute the greater part of the so-called "carbolic acid" of disinfecting powders. For their detection, the test with dilute sodium hydroxide will usually be found sufficient. In other cases the crude carbolic acid should be treated with twice its volume of a 20% sodium hydroxide solution (1.2 sp. gr.), any undissolved oils separated, and the alkaline solution shaken with ether to remove any neutral oils still remaining dissolved. The ethereal layer is separated, added to the neutral oils previously obtained, the ether driven off by a gentle heat, and the residual neutral oils or naphthalene measured or weighed. The alkaline solution of the phenols is boiled in a small flask to drive off the ether, and acidified in a narrow, graduated tube or a burette with diluted sulphuric acid (1:3), and the layer of separated phenols is measured.

DIHYDROXYBENZENES. DIHYDRIC PHENOLS

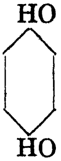
The substitution of 2 hydrogen atoms in benzene by hydroxyl will give rise to 3 isomeric forms, exactly analogous in structure to the xylenols and cresols described in the preceding pages.



Catechol, Pyrocatechin
(ortho-; 1–2)



Resorcinol, Resorcin
(meta-; 1–3)



Hydroquinone, Quinol
(para-; 1–4)

All 3 forms are commonly known. They were originally obtained from natural products by destructive distillation, but are now mostly prepared from benzene by synthetic methods. When the mono-halogenphenols (*e. g.*, C_6H_4ClOH), phenolsulphonates, or benzene-disulphonates are fused with potassium hydroxide, the corresponding dihydroxy-benzene is usually obtained, but the reaction is sometimes irregular, the meta-form being often produced when one of the isomerides is expected. The nature of the reactions is shown by the following equations:

$$\begin{aligned}
C_6H_4I(OH) &+ K(OH) = C_6H_4(OH)_2 + KI, \\
C_6H_4(OH)SO_3K &+ K(OH) = C_6H_4(OH)_2 + K_2SO_3, \\
C_6H_4(SO_3K)_2 &+ 2K(OH) = C_6H_4(OH)_2 + 2K_2SO_3.
\end{aligned}$$

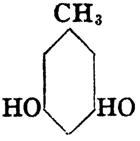
If the temperature be high, resorcinol is always obtained, as it is more stable than its isomers.

The 3 dihydroxybenzenes are volatile crystallisable bodies, readily soluble in water, alcohol, and ether, and extracted from their aqueous solutions by agitation with ether. They form ethers when their hydrogen is displaced by alkyl-radicals, and resemble glycols in many respects.

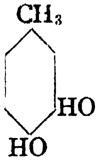
Like the monohydric phenols they are weakly acid in character, dissolving in alkalies with replacement of their hydroxyl hydrogen by metal. The dissociation constants of their first hydroxyl is slightly greater than phenol, whilst the second hydroxyl shows a considerably lower constant. Quinol shows a dissociation constant of 1.75×10^{-10} for the first hydrogen and 3.97×10^{-12} for the second. Their m. p. and b. p. are much higher than those of the corresponding monohydric phenols.

The three isomeric forms show characteristic differences in chemical and physical properties. Some of the chief distinctions between the three dihydroxybenzenes are shown in the following table:

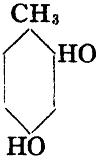
The *homologues* of the dihydroxybenzenes have as yet little importance. 6 dihydroxytoluenes are possible, of which the following four are best known:



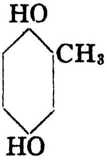
Orcinol, Orcin (1–3–5)



Homocatechol (1–3–4)



Isorcinol (1–2–4)



Toluhydroquinone (1–4)

In toluhydroquinone the methyl group may be assumed to be at either 2, 3, 5, or 6, without changing the stereochemical relations. The methyl ether of homocatechol, $C_6H_3(OCH_3)(CH_3)(HO)$, is known as *creosol* (not to be confounded with cresol) and is found in beechwood tar (see page 342).

Resorcinol. Resorcin. Metadihydroxybenzene

Resorcinol was originally obtained by the action of fused alkalies on certain resins, and subsequently by their action on meta-iodophenol. It is now manufactured on a large scale by heating sodium hydroxide with sodium meta-benzenedisulphonate. The fused mass is allowed to cool, dissolved in water, and the solution acidified. From the solution the resorcinol is extracted and purified by distillation under reduced pressure.

Resorcinol crystallises in rhombic prisms from water, alcohol, and ether, but in needles from benzene. The crystals gradually become pink, and appear phosphorescent when struck or rubbed in the dark. The odour is peculiar and the taste sweetish bitter.

Resorcinol is soluble at 20° in an equal weight of water or in 0.312 parts by weight of alcohol. It dissolves in 20 parts of benzene at 60°. Resorcinol has a bactericidal action about three times that of phenol.

Resorcinol is important medicinally and as a dye intermediate. The medicinal grade is specified by the United States Pharmacopœia (9th Edition, 1916) as follows:

"Resorcinol occurs in colourless, or nearly colourless, needle-shaped crystals, or as a powder, having a faint, peculiar odour and a sweetish, followed by a bitter, taste. It acquires a pink tint on exposure to light and air.

"1 grm. of resorcinol dissolves in 0.9 mil of water and in 0.9 mil of alcohol at 25°; also in about 0.2 mil of water at 80°; freely soluble in glycerin or ether; slightly soluble in chloroform.

"Its aqueous solution (1 in 20) is neutral or only faintly acid to litmus.

"It melts between 109° and 111°.

"The addition of a few drops of ferric chloride T. S. to 10 mils of an aqueous solution of resorcinol (1 in 200) produces a bluish-violet colour, changing to brownish-yellow on the addition of ammonia water (distinction from catechol and quinol).

"Dissolve 0.1 grm. of resorcinol in 1 mil of potassium hydroxide T. S. and then add a drop of chloroform; the mixture upon being heated assumes an intense, crimson colour, and if a slight excess of hydrochloric acid is then added, the colour changes to a pale straw-yellow.

"Incinerate about 2 grm. of resorcinol; not more than 0.5% of ash remains.

"Lead acetate T. S. produces no precipitate when added to an aqueous solution of Resorcinol (1 in 20) (catechol).

"An aqueous solution of Resorcinol (1 in 20) does not emit the odour of phenol when gently warmed.

"Dissolve about 1.5 grm. of Resorcinol, accurately weighed, in sufficient distilled water to make 500 mils. Transfer 25 mils of the solution to a 500 mil glass-stoppered flask having a long and narrow neck, add 50 mils of tenth-normal bromine V. S., and dilute with 50 mils of distilled water. Then add 5 mils of hydrochloric acid and at once stopper the flask. Shake the liquid and allow it to stand for one minute, then dilute it with 20 mils of distilled water, add 5 mils

	Catechol, pyrocatechin ortho- (1:2)	Resorcinol, resorcin meta- (1:3)	Quinol, hydroquinone para- (1:4)
Chief modes of formation	Fusion of phenol ortho-derivatives, kino, benzoin or guaiacum, with caustic alkalies. Dry distillation of protocatechuic acid. Action of hydrogen iodide at 200° on guaiacol.	Fusion of phenol meta-derivatives, galbanum, asafœtida, etc., with caustic alkalies. Dry distillation of extract of brazil-wood. On the large scale from benzenedisulphonic acid.	Fusion of phenol para-derivatives with alkali hydroxides. Dry distillation of quinic acid. Hydrolysis of the glucoside arbutin, by dilute sulphuric acid. Reduction of quinone by aqueous sulphurous acid.
Appearance and crystalline form	Rhombic prisms or thin pearly plates.	Rhombic prisms or plates.	Hexagonal prisms or monoclinic plates.
Sp. gr.	1.344.	1.272.	1.330.
Action of heat	Melts at 104°; boils at 245°; may be sublimed, forming pungent fumes which excite coughing.	Melts at 110°; boils at 276°; distils almost unchanged. Sublimes in silky needles.	Melts at 169°; sublimes when carefully heated, but decomposes if heated slowly.
Solubility	Very soluble in water, alcohol, and ether; extracted by ether from aqueous solutions.	Soluble in less than equal weight of cold water, very soluble in hot water; very soluble in alcohol, ether, and glycerin; extracted by ether from aqueous solutions. Nearly insoluble in chloroform, carbon disulphide, and cold benzene.	Soluble in 17 parts of cold water, very soluble in hot water. Very soluble in alcohol and ether; extracted by ether from aqueous solutions. Difficultly soluble in benzene.
Behaviour of aqueous solution with reagents:			
(*a*) Exposed to air in presence of alkali	Becomes green, brown, and black.	Turns brown.	Turns brown.
(*b*) Colouration with ferric chloride (avoiding excess).	Dark green, changed to violet-red by ammonium hydroxide or acid sodium carbonate.	Dark violet, destroyed by ammonium hydroxide.	Forms green crystals of quinhydrone, changed to yellow, sparingly soluble quinone by excess of the reagent.
(*c*) Reaction with lead acetate	White precipitate.	No precipitate.	No precipitate unless ammonium hydroxide be added.
(*d*) Reaction with silver nitrate	Reduction of metallic silver in the cold.	No reaction in the cold; metallic silver reduced on boiling or on addition of ammonium hydroxide.	Metallic silver reduced on warming.
Taste of aqueous solution	Bitter.	Sweetish.	Sweetish.

of potassium iodide T.S. and allow it to stand for five minutes. The titration of the liberated iodine with N/10 sodium thiosulphate V.S., starch T.S. being used as indicator, shows not less than 99.5% of $C_6H_4(OH)_2$.

"Each mil of N/10 bromine V.S. corresponds to 0.001834 grm. of $C_6H_4(OH)_2$. Each grm. of Resorcinol corresponds to not less than 542.5 mils of N/10 bromine V.S."

According to Berthelot and Michel (*Bull. sci. pharmacol*, 1919, **26**, 401) the three dihydroxybenzenes give characteristic colours with the sodium salt of p-toluenedisulphochloroamide (chloramine T). 1 c.c. of a cold saturated solution of this reagent with 4 c.c. of a 10% solution of resorcinol gives a green colour changing to yellow. Cathechol gives an amethyst colour and quinol a current red changing to brown. The reactions of resorcinol and catechol are very delicate.

On adding bromine water to an aqueous solution of resorcinol, *tribromoresorcinol*, $C_6HBr_3(OH)_2$, is thrown down as a white flocculent precipitate consisting of crystalline needles, closely resembling tribromophenol.

A neutral or slightly acid solution of resorcinol treated with a few drops of 10% copper sulphate solution and an equal volume of 10% potassium cyanide, gives on agitation and dilution to a yellow-red colour (following an intermediate red colour) a distinct fluorescence. Volay, Boucher and Girard state that this reaction is delicate to a concentration of 0.1 grm. of resorcinol per litre.

A solution of resorcinol treated with a mixture of equal parts of 40% formaldehyde and hydrochloric acid gives a white cloudiness which produces a carmine precipitate on boiling.

Kraushopf and Ritter (*J. Amer. Chem. Soc.*, 1916, **38**, 2182) have observed that resorcinol may be detected in the presence of relatively large quantities of catechol and quinol by its reaction with an ammoniacal cobalt solution. 1 c.c. of solution containing 1% of resorcinol is treated in a Nessler tube with 1 c.c. of a cobalt chloride solution (0.0004 grm. cobalt per c.c.), 0.3 c.c. of strong ammonium hydroxide, 3 c.c. of 95% alcohol and water to make 50 c.c. The tube is stoppered and let stand for five minutes and shaken. A deep green colour is produced which is not obscured by the brown colour given by catechol and quinol.

With hypochlorites, resorcinol gives a violet, catechol an evanescent green, and quinol slowly develops a yellowish-red coloration.

When treated with excess of nitric acid, resorcinol is converted into a trinitroresorcinol, $C_2H(NO_2)_2(OH)_2$, 2:4:6. This substance formerly called styphnic or oxypicric acid, forms sulphur-yellow hexagonal crystals, m.p. 175°. It closely resembles picric acid, except that it is astringent instead of bitter.

When resorcinol is heated with excess of phthalic anhydride to about 200° for half an hour, the mixture acquires a yellowish-red colour, and contains the resorcinolphthalein or fluorescein, $C_{20}H_{12}O_5$. If the melt be dissolved in dilute sodium or ammonium hydroxide, the presence of resorcinol becomes apparent by the production of a dark red solution changing on dilution to reddish-yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colourless by transmitted light. On acidifying the solution and agitating with ether, the fluorescein is taken up, and will be again dissolved on agitating the ethereal solution with soda. When similarly treated, *phloroglucinol* yields a yellow and *pyrogallol* a blue liquid, neither of which is fluorescent. The blue colour due to pyrogallol may be destroyed by cautious addition of potassium permanganate, which acts only slowly on the fluorescein. Catecholphthalein, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in alkaline hydroxide solution with fine blue colour. Quinizarin, formed in a similar manner from quinol, dissolves in alkalies with violet-blue colour, and if the solution be acidified with sulphuric acid it becomes red, and the quinizarin may be extracted by agitation with ether and recovered from the ethereal solution by shaking with sodium hydroxide solution, which acquires a violet-blue colour.

When resorcinol is fused with excess of sodium hydroxide, phloroglucinol and some diresorcinol are produced.

Other properties and reactions of resorcinol are described on page 280.

Estimation of Resorcinol.—Resorcinol is estimated by means of its reaction with bromine by a method very similar to that described for phenol on page 281. The details of the method for resorcinol as contained in the United States Pharmacopœia have been given on page 334.

Quinol. Hydroquinone. p-Dihydroxybenzene

Some of the properties and reactions of quinol have been described on page 280. This substance is of great importance on account of its wide use as a photographic developer. It occurs in certain plant exudations and can be made by the distillation of certain resins. It is manufactured, generally, by the oxidation of aniline to quinone with chromic acid and the reduction of the quinone with sulphurous acid, giving quinol.

Quinol is soluble in 17 parts of water at 20°.

J. Pinnow (*Z. anal. Ch.* 50, 154) has suggested the estimation of quinol by its reduction of Fehlings solution.

Catechol. Pyrocatechin. o-Dihydroxybenzene

Catechol and its derivatives occur quite widely in the plant kingdom. It may be prepared by heating protocatechuic acid or other of its derivatives or by the action of hydrogen iodide on guaiacol or on the wood creosote fraction containing it. It is made synthetically by the action of caustic alkali on *o*-phenol-sulphonic acid or on *o*-chlorophenol.

Some of the properties and reactions of catechol have been referred to on page 335.

Catechol forms short, square prisms or thin, pearly plates, resembling benzoic acid. It sublimes readily and condenses in brilliant laminæ. The taste is bitter, and the fumes are pungent and excite coughing.

The aqueous solution of catechol rapidly turns brown.

Catechol forms unstable compounds with bases. With lime-water an aqueous solution of catechol gives a reddish or brown colour, but the solution remains clear for some time. Alkali hydroxides behave similarly to lime-water, the solution becoming, in succession, green, brown, and black. Catechol is not precipitated by gelatin or alkaloids. With lead acetate it yields a white precipitate, which is easily soluble in acetic acid. Catechol reduces silver nitrate at ordinary temperatures and Fehling's solution on warming.

An aqueous solution of catechol gives no reaction with ferrous salts. With ferric chloride, avoiding excess, it gives a grass-green coloration, which on addition of acid sodium carbonate is changed to a fine violet-red, not much altered by boiling, but restored to green on the cautious addition of sodium hydroxide. (These reactions distinguish catechol from pyrogallol.) Pine-wood moistened with hydrochloric acid mixed with a solution of catechol acquired a violet-blue colour. Phloroglucinol gives a similar reaction.

Millon's reagent gives with catechol a precipitate of a dark slate colour.

Catechol in the absence of other reducing agents may be determined with a fair degree of accuracy, according to C. M. Pence (*J. Ind. Eng. Chem.*, 1913, **5**, 218), by treatment with an excess of standard potassium permanganate in a solution alkaline with sodium hydrogen carbonate, acidification, reduction of the excess permanganate with potassium iodide and titration of the iodine liberated. The same method applies to resorcinol, quinol, pyrogallol, salicylic acid, salol and other substances.

Catechol can also be estimated colorimetrically by comparison of the violet coloration which it gives with osmium tetroxide with that given of a standard solution of pure catechol (Mitchell, *Analyst*, 1924, **49**, 162).

Homocatechol or Methylcatechol occurs as a methyl-ether in wood-tar creosote, and may be obtained therefrom by boiling with with hydrobromic or hydriodic acid. Homocatechol is a syrupy liquid, which dissolves readily in water, alcohol and ether, but not in benzene (distinction from catechol). It reduces silver nitrate and Fehling's solution in the cold. With ferric chloride, homocatechol gives a green coloration, which is changed to reddish-violet on cautious addition of ammonia or sodium hydrogen carbonate.

Ethers of Catechol and Homocatechol.—By suitable means 1 or both the hydrogen atoms of the hydroxyl-groups of catechol and homocatechol can be replaced by alkyl-radicals. Thus, the following methyl ethers can be obtained:

Catechol.

$$C_6H_4\left\{\begin{matrix}OH\\OH.\end{matrix}\right.$$

Methyl catecholate. Catechol methyl-ether. Guaiacol.

$$C_6H_4\left\{\begin{matrix}OCH_3\\OH.\end{matrix}\right.$$

Dimethyl catecholate. Catechol dimethyl-ether. Veratrol.

$$C_6H_4\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$$

Homocatechol. Methylcatechol.

$$C_6H_3(CH_3)\left\{\begin{matrix}OH\\OH.\end{matrix}\right.$$

Methyl homocatecholate. Homocatechol methyl-ether. Creosol.

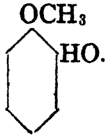
$$C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OH.\end{matrix}\right.$$

Dimethyl homocatecholate. Homocatechol dimethyl-ether.

$$C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OCH_3.\end{matrix}\right.$$

Guaiacol, creosol, and homocatechol dimethyl-ethers form the greater part of the fraction of beechwood-creosote boiling between 200° and 220°. Veratrol is also very probably present. The dimethyl-ethers shown above can be prepared from guaiacol and cresol, respectively, by dissolving these substances in a strong solution of potassium hydroxide in methyl alcohol and boiling with methyl iodide. They are distinguished from the monomethyl ethers by their insolubility in aqueous solutions of alkali hydroxides, and by giving no green or blue coloration with ferric chloride. Both the mono- an dimethyl ethers can be demethylated by heating them with excess of a halogen-acid, catechol and homocatechol being thereby formed.

Guaiacol. Methyl catecholate. Catechol methyl ether,



This substance has attracted much attention on account of its vogue as a remedy in tuberculosis. It is prepared from beechwood creosote by treating the fraction which distils between 200° and 205° with an alcoholic solution of potassium hydroxide by which potassium guaiacol is formed, and this is converted into guaiacol by the action of dilute acids. Guaiacol may also be prepared by several synthetic methods, as when catechol (1–2 dihydroxy benzene) is heated with equivalent quantities of potassium methyl sulphate and potassium hydroxide or sodium hydroxide. The action is:

$$C_6H_4(OH)_2 + K(CH_3)SO_4 + KOH = C_6H_4(OCH_3)(OH) + K_2SO_4 + H_2O.$$

Pure guaiacol was formerly described as a liquid, but was obtained by Béhal and Choay (*Comp. rend.*, 1893, **116**, 197) as a white solid which, when crystallised from petroleum spirit, is obtained in hard, uniaxial, dihexagonal prisms. Guaiacol melts at temperatures variously stated at 28.5° to 33°, and boils at 204° to 205°. When melted, guaiacol remains indefinitely in a state of super-fusion, and may even be cooled to —2° without solidifying; but on addition of a crystal of the solid substance the whole immediately crystallises, the temperature rising to 27°. The sp. gr. of liquid guaiacol at 0° is 1.1543, and at 15° from 1.143 to 1.149.

Guaiacol dissolves in water at 25° to the extent of only 1.89 grm. per 100 grm. of water. It dissolves readily in most organic solvents, including anhydrous, but not aqueous glycerin.

It is also soluble in solutions of alkali hydroxides, and with an alcoholic solution of potassium (not sodium) hydroxide forms a crystalline mass of the potassium derivative. The same compound speedily separates on mixing equal measures of guaiacol and aqueous potassium hydroxide solution of 1.3 sp. gr. Impure guaiacol, even if containing 70% of the real compound, remains liquid under the same conditions.

Guaiacol has a sweet taste, and when placed on the tongue melts and produces a feeling of intense astringency, but it is without action on the mucous membrane. It is somewhat less toxic than phenol or catechol. It has a bactericidal action slightly less than phenol.

When treated in aqueous solution with ferric chloride, guaiacol gives a brownish turbidity; but if ferric chloride (avoiding excess) be added to a 1% solution of guaiacol in alcohol, a fine blue coloration is obtained, rapidly changing to green and yellow.

The following tests for guaiacol are given in the United States Pharmacopæia.

"Guaiacol is a colourless or yellowish, strongly refractive liquid, or a colourless or yellowish, crystalline solid, having an agreeable, aromatic odour. It becomes darker on exposure to light and air. The solid form when liquefied may remain so for some time, even at a low temperature.

"One grm. of guaiacol dissolves in 53 mils of water and in 0.8 mil of glycerin at 25°, but separates from the glycerin on the addition of water; miscible with alcohol, chloroform, ether or acetic acid.

"The specific gravity of liquid guaiacol is between 1.110 and 1.114 at 25°.

"Solid guaiacol melts at about 28°."

"Not less than 85% of guaiacol distils between 200° and 210°.

"The addition of a drop of ferric chloride T. S. to 10 mils of an alcoholic solution of guaiacol (1 in 100) produces an immediate blue colour, changing to emerald-green, and finally becoming yellowish.

"Incinerate about 1 grm. of guaiacol; not more than 0.1% of ash remains.

"Shake 2 mils of liquefied guaiacol with 4 mils of purified petroleum benzine; the mixture separates on standing into two distinct, clear layers. Permanent turbidity or failure to separate into layers indicates the presence of impurities.

"One mil of liquefied guaiacol dissolves in 2 mils of potassium hydroxide solution (15%), when heated for one minute in boiling water; on cooling, it congeals to a nearly white mass. Much coloration or failure to congeal indicates the presence of impurities. The mass thus obtained forms a clear solution with 20 volumes of distilled water (turbidity indicates oily hydrocarbons)."

A test for guaiacol is given by R. Huerre (*Bull. sci. pharmacol.*, 1922, **29**, 180) who treats 1–2 drops of guaiacol in 10 c.c. water with 7 drops of nitric acid, obtaining an intense red colour. Catechol gives a similar reaction. The di-ethers of catechol and homopyrocatechol give crystalline nitration products.

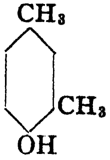
The estimation of guaiacol is described under "Wood-creosote."

Commercial guaiacol is of very variable quality, some specimens being stated to contain not more than 30% of the pure substance, but good samples contain fully 90%. Inferior samples have a low sp. gr.—*e. g.*, 1.046—but those rich in guaiacol have a gravity approaching that of the pure substance. Pure guaiacol requires 8 times its volume of cold, petroleum spirit for solution, but many commercial specimens are soluble in 4 volumes or even less.

According to Marfori (*Gazzetta*, 1890, **20**, 537), the solubility of guaiacol in water is notably reduced by the presence of impurities. Heated with chloroform and solid potassium hydroxide, pure guaiacol gives a purple-red coloration, whilst the impure product gives a less marked reaction. Marfori states that the pure substance gives with concentrated sulphuric acid a stable purple red coloration, whilst the least impurity detracts from the purity of the colour formed. On the other hand, some observers state that pure guaiacol gives no colour, or only a slight yellow, with cold strong sulphuric acid.

Creosol

Homocatechol Methyl Ether,



This substance is homologous with guaiacol, and occurs in the fraction of beechwood creosote boiling at about 220°. When freshly distilled, it is a colourless liquid, having a pleasant odour of vanilla, especially when dilute. It dissolves in aqueous alkalies, and with a strong solution of potassium hydroxide in alcohol sets to a mass of needles of the potassium compound, $C_8H_9O.OK + 2H_2O$. A solution of creosol yields a metallic mirror when warmed with silver nitrate, and gives a green coloration with ferric chloride. Creosol differs from guaiacol in its higher b. p. (219°), in not crystallising, and in its greater solubility in petroleum spirit. In its therapeutic effects creosol appears to present a close resemblance to guaiacol.

Creosol methyl ether, or *dimethyl homocatecholate*, $C_6H_3(CH_3):(OCH_3)_2$, also occurs in beechwood creosote. It boils at 218°, gives no coloration with ferric chloride, and is insoluble in aqueous solutions of alkali hydroxides.

WOOD-CREOSOTE

Wood-creosote is essentially a mixture of the ethers of the polyhydric phenols. It is produced from wood tar resulting from the destructive distillation of hardwoods such as beech, maple, birch and oak. This tar on distillation yields a heavy oil fraction containing 20% to 80% of phenolic substances soluble in sodium hydroxide solution. The probable average content of these substances in the heavy oil is about 60%. For the preparation of creosote, the heavy oil is extracted with sodium hydroxide solution, the aqueous extract boiled or steam distilled in contact with air to remove or oxidise neutral oils and acidified. The phenolic layer is separated, distilled and reextracted with caustic soda. This treatment is repeated generally several times. The final creosote is the fraction passing over between 200 and 220°. The best grade of creosote is made from beechwood tar.

The composition of wood creosote varies considerably. A sample of beechwood creosote investigated by Behal and Choay (*Compt. rend*, 1894, **119**, 166) showed the following composition:

Phenol	5.2%
o-Cresol	10.4%
m- and *p*-Cresols	11.6%
o-Ethyl-phenol	3.6%
Xylenols	3.0%
Guaiacol	25.0%
Cresol and homologues	35.0%
Other phenols	6.2%

Among other compounds which have been identified in wood creosote are the dimethyl ethers of pyrogallol and of methyl- and propylpyrogallol. These compounds have been identified both in beechwood and in maplewood creosote. Dimethylguaiacol and propylguaiacol are present in insignificant proportions, but the latter substance is highly objectionable, since a single drop causes bleeding, when placed on the tongue. Hence purified creosote should be absolutely free from this constituent, the presence of which may be recognised by the blue coloration produced with baryta water.

Smith and Acree (*J. Ind. Eng. Chem.*, 1917, 9, 275) give the following results of a fractional distillation of a sample of beechwood creosote:

Fraction	Temperature, °C.	Fraction, %	Total, %	Sp. gr. 60° F.	Refractive index 60° F.	Character of fraction
1	205	3.7	3.7		..	Yellow liquid
2	215	10.1	13.8	....	.....	Golden yellow liquid
3	225	20.8	34.6	1.003	1.5074	Golden yellow liquid
4	235	8.1	42.7	1.009	1.5083	Golden yellow liquid
5	245	5.5	48.2	1.012	1.5111	Golden yellow liquid
6	255	8.4	56.6	1.019	1.5117	Golden yellow liquid
7	265	13.4	70.0	1.021	1.5123	Golden yellow liquid
8	275	2.7	72.7	1.002	1.5138	Golden brown liquid
9	285	4.8	77.5	.....	1.5138	Red-brown paste
10	...	21.6	99.1	.....	......	Residue: black solid

Wood-creosote is a strongly refracting liquid which is colourless when freshly distilled, but acquires a yellow or brown colour on keeping. It has a peculiar, persistent, smoky, aromatic odour, distinct from that of phenol. The sp. gr. ranges between 1.040 and 1.087. Wood-creosote is not solidified by moderate cold. It is a powerful antiseptic, but does not coagulate albumin. It preserves animal matters without causing disintegration, as phenol is liable to do, and is less powerfully caustic than that substance.

Wood-creosote is only slightly soluble in water, but is rendered anhydrous with difficulty. Like absolute phenol and cresol, it is miscible in all proportions with alcohol, ether, glacial acetic acid, chloroform, benzene, and carbon disulphide. It dissolves in concentrated sulphuric acid to a red liquid, which slowly changes to purple-violet. Shaken with concentrated hydrochloric acid, in the absence of air, wood-creosote becomes red, the colour changing in contact with air to dark brown or black. Wood-creosote is violently attacked by nitric acid. With bromine water it forms a derivative of a reddish colour.

Wood-creosote is soluble in solutions of alkali hydroxides, and forms a crystalline compound with potassium hydroxide, but not with sodium hydroxide.

The United States Pharmacopœia furnishes the following with respect to creosote:

"Creosote is an almost colourless or yellowish, highly refractive, oily, liquid, having a penetrating, smoky odour, and a burning caustic taste; it does not readily become brown on exposure to light.

"Creosote is slightly soluble in water; it is miscible with alcohol, ether, or fixed or volatile oils.

"It is neutral or faintly acid to litmus.

"Specific gravity: not below 1.073 at 25°.

"It begins to distil between 195° and 200°, and not less than 80% by volume distils between 200° and 220°.

"Creosote is inflammable, burning with a luminous, smoky flame.

"Add 1 drop of ferric chloride T. S. to 10 mils of a saturated aqueous solution of creosote; the liquid develops a violet-blue colour, which is very transient; it then clouds almost instantly, the colour passing rapidly from a grayish-green to a muddy brown, with finally the formation of a brown precipitate.

"Mix equal volumes of creosote and collodion in a dry test tube; no permanent coagulum is produced (phenol and so-called "coal-tar creosote").

"Mix 4 mils of creosote with 4 mils of glycerin; a clear mixture results, from which a creosotic layer, equal to or greater in volume than the creosote taken, separates on the addition of 1 mil of water ("coal-tar creosote").

"Two mils of creosote requires not less than 10 mils nor more than 18 mils of normal sodium hydroxide V. S. to produce a clear liquid. This liquid remains unclouded on diluting with 50 mils of distilled water (hydrocarbons and bases).

"Shake gently 1 mil of creosote with 2 mils of petroleum benzine and 2 mils of freshly prepared barium hydroxide T. S., until a uniform mixture is produced. Upon complete separation three distinct layers are visible; a middle layer containing the creosote, a benzine layer which is neither blue nor muddy, and an aqueous layer which does not acquire a red tint (coerulignol and some other high-boiling constituents of wood-tar)."

Creosote is commonly stated to be optically active. The British Pharmacopœia of 1885 alleged that it was dextro-rotatory, while the edition of 1898 asserts that it is levo-rotatory, both statements being misleading. As a rule, wood creosote exhibits no sensible optical activity, and the same is true of pure guaiacol and creosol. Occasionally, specimens of creosote are met with which exhibit an insignificant activity, but the character is valueless as a practical test.

Wood-creosote of good quality has an agreeable, vanilla-like odour, and darkens in a marked manner on prolonged exposure to light.

An alcoholic solution of wood creosote should not give any coloration whatever (neither blue nor reddish) with barium hydroxide. The test may be made by dissolving the creosote in twice its volume (or a sufficiency) of petroleum spirit which should form a perfectly clear solution; and on shaking this liquid with an equal volume of saturated baryta water no blue, violet, or red colour should appear in either stratum. Such colours indicate the presence of *coerulignol* or other objectionable impurities.

Wood-creosote is practically insoluble in strong solution of ammonium hydroxide, and when shaken with 1 or 2 volumes thereof (sp. gr. 0.880) the mixture separates on standing into 2 layers, of which the lower or creosotic layer considerably exceeds the volume of the sample used. Genuine and pure wood creosote, when agitated with ammonium hydroxide, will not acquire a colour deeper than lemon-yellow in half an hour, and the upper aqueous stratum should be pale or yellowish. In 24 hours the creosote should have acquired a brown or olive-green tint—not blue.

The following method may be employed for the separation of the phenoloid constituents of wood-creosote boiling between 195° and 240°, and; might be used for the detection and estimation of coal-tar acids purposely added: The sample is dissolved in twice its volume of ether, and the solution shaken with a 5% solution of potassium hydroxide, which dissolves the phenolic substances. The alkaline liquid is separated, acidulated with hydrochloric acid, and shaken up with ether. The phenoloid oils obtained on evaporating the ethereal solution are distilled, mixed with half their volume of ether, and twice their volume of a saturated alcoholic solution of potassium hydroxide. Creosol and guaiacol are converted into crystalline potassium compounds, while the similar compounds of phenol and cresol remain in solution. The crystalline pulp is pressed through a cloth, the filtrate evaporated, the residue treated with water, and the solution acidified with hydrochloric acid. The liberated phenols are retreated with ether and alcoholic potassium hydroxide, the process being repeated, if necessary, so long as crystals are deposited in the cold, when the phenols are once more liberated, and may be weighed, measured, or titrated with bromine. The crystals may be dissolved in water and the solution decomposed by hydrochloric acid, when the guaiacol, cresol, and higher homologues are liberated, and may be purified and separated by fractional distillation. (Tiemann and Koppe, *Ber.*, 1881, 2005.)

Phenol is detected, according to M. E. Merklen (*Zeits. anal. Chem.*, 1901, **40**, 621–3), as follows: 4 c.c. of creosote are heated with 1 c.c. of ammonia to 60°. The mixture is spread over the surface of a large basin and subjected to the action of bromine vapour. If phenol is present, a blue coloration is obtained. Pure creosote gives a brown or green colour.

In consequence of the large demand of recent years for guaiacol and its preparations, much of the wood-creosote now sold has been deprived of its guaiacol, so that it is now rare to find specimens containing even 20% of that constituent.

Quantitative Estimation of Wood-creosote

Béhal and Choay (*Comp. rend.*, 1893, **116**, 197) have devised a method for the estimation of guaiacol in wood-creosote, based on the following principles: 1. Treatment of the sample with hydrobromic acid, whereby the methyl ethers of the polyphenols are completely demethylated. Thus, guaiacol by such treatment yields catechol, and creosol gives homo- or methyl-catechol. 2. Distillation of the demethylated oil in a current of steam, whereby the monophenols (phenol, cresols, xylenols) are carried over and are thus separated from the polyphenols. 3. Extraction of catechol, homocatechol, and any traces of unvolatilised monophenols by ether. 4. Separation of catechol from homocatechol by treatment with benzene, which dissolves the former substance only. The following are the working details of the process as modified by M. Adrian (*Nouv. Rem.*, **13**, 97; Abst. *J. Soc. Chem. Ind.*, 1897, 367): 100 grm. weight of guaiacol or creosote are placed in a flask of 250 c.c. capacity, connected, on the one hand, with another flask which serves as a generator of gaseous hydrogen bromide (generated by the action of water on phosphorus tribromide) and on the other with an inclined reflux condenser. The exit-tube from the condenser leads the gas through 2 wash-bottles containing water. The delivery tube between the generator and the guaiacol is furnished with a large bulb to prevent aspiration of the liquid when cooling. The gas is allowed to pass slowly through the guaiacol, which is gently warmed after the process has been in operation for half an hour, and continued for 90 minutes. It is then cooled, transferred to a large flask, diluted with 5 or 6 volumes of water, and all volatile substances removed by steam distillation. When no more oily liquid comes over, the distillation is stopped, the catechol in the residual liquor extracted, together with homocatechol, by washing out with ether, the ether cautiously distilled off, and the residue dried. This is then treated with dry benzene, which extracts the whole of the catechol produced by demethylation of the guaiacol originally present, leaving the homocatechol undissolved. From the solution of benzene the catechol is crystallised out and weighed. Care must be taken at the end of the process to avoid the least trace of moisture in the residue and in the solvent, or crystallisation will not take place; and even with perfectly dry benzene the mother-liquor must be concentrated and the catechol which crystallises out added to the main quantity.

The monophenols which distil with steam are separated by Béhal and Choay by fractionation and subsequent conversion into benzoates. The methyl derivatives of the diphenols are separated by precipitation with strontium hydroxide, the precipitate being decomposed by hydrochloric acid. They are then fractionated, and, if necessary, converted into carbonates by carbon oxychloride, and further separated by fractional crystallisation.

L. F. Kebler (*Amer. Jour. Pharm.*, 1899, 409) has described the following process of estimating guaiacol in creosote: 5 c.c. of the sample are mixed with 50 c.c. of a 20% solution of potassium hydroxide in alcohol. The crystalline mass of the potassium derivatives of guaiacol and creosol, which forms in the course of ½ hour, is pressed between filter-paper until dry and treated in a test-tube with 5 c.c.

of 20% sulphuric acid. On heating the mixture, the guaiacol and creosol rise to the surface. The liquid is then diluted with sufficient water to cause the oily layer to sink, when the aqueous portion is decanted and the oil treated with 4 c.c. of concentrated ammonium hydroxide. A hard crystalline compound is immediately formed by the guaiacol, and a semi-crystalline mass is given after some time by the creosol. On treating the crystalline mixture with petroleum spirit, all but the ammonium compound of guaiacol is dissolved, and this can be purified by filtration and washing with petroleum spirit. The compound is then decomposed by dilute sulphuric acid, the liberated guaiacol extracted by agitation with petroleum spirit, and the solution evaporated in a tared flask.

A useful indication of the proportion of guaiacol present in wood-creosote is afforded by the sp. gr. of the sample, or preferably of the fraction distilling between 200° and 205°. The specimens having the highest sp. gr. are richest in guaiacol.

Adulterations of Wood-creosote.—Wood creosote has been sometimes adulterated with, or wholly substituted by, the crude phenols of coal-tar. The reactions of the cresols and xylenols resemble those of wood creosote still more closely than do those of phenol, and many of the proposed tests for differentiation are valueless.

The reactions described below were carefully studied by Allen on specimens of pure phenol, Calvert's No. 5 carbolic acid (representing cresols), and Morson's creosote. The descriptions should be compared with the reactions of phenol and cresol.

a. Wood-creosote is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose. Shaken with half its volume of collodion, Calvert's No. 5 carbolic acid coagulates the guncotton to a transparent jelly, best observed by inclining the tube and causing the liquid to flow gently from one end to the other. Morson's creosote does not precipitate the nitrocellulose from collodion, but mixes perfectlywith the ethereal solution Addition of much wood creosote to a mixture of collodion and a coal-tar acid causes a re-solution of the precipitated nitrocellulose. When a mixture of equal volumes of Morson's creosote and Calvert's No. 5 carbolic acid is shaken with half its volume of collodion, decided signs of precipitation are observed. With ⅔ of the coal-tar acids to ⅓ of creosote, the precipitation of nitrocellulose is very marked.

b. When carefully used, a solution of ferric chloride affords a very satisfactory means of distinguishing wood-creosote from coal-tar acids, but not for distinguishing either in mixtures of the two. The reaction produced varies, however, in a somewhat curious manner, according to the way in which the test is performed, the following being, the most satisfactory methods of operating: 1. On placing a a drop of Morson's wood creosote in a hemispherical porcelain dish and adding a few drops of neutral solution of ferric chloride, a yellowish-brown coloration is produced, and on stirring the undissolved creosote acquires a reddish-brown and the ferric solution an olive-brown tint. Calvert's No. 5 carbolic acid, when similarly treated, acquires a light straw-colour, whilst the ferric solution assumes a fine violet coloration, which is permanent. On slightly diluting the mixtures with alcohol they both yield olive-brown solutions, but on further addition of alcohol the creosotic mixture becomes a light olive-brown tint with a shade of green whilst the carbolic solution turns light brown or amber without any green tinge. 2. On the other hand, if a drop of wood creosote be dissolved in 10 drops of alcohol, and a drop or two of dilute ferric chloride added, a bluish-green coloration is produced, changing to a fine green, while Calvert's No. 5 carbolic acid yields a greenish-blue colour under similar conditions. On adding sufficient ferric chloride to precipitate the wood creosote from its solution, an olive-brown coloration changing to deep brown is obtained; whilst the carbolic mixture retains its greenish-blue tint, though more or less disguised by the yellow colour of the ferric solution. 3. The addition of 1 drop of a 10% aqueous solution of ferric chloride to 15 c.c. of an aqueous solution of wood creosote produces a green coloration, changing very rapidly to brownish-yellow. The solution of a coal-tar acid when similarly treated gives a permanent violet-blue coloration.

c. Morson's wood creosote is sharply distinguished from the coal-tar acids by its insolubility in absolute glycerol (sp. gr. 1.258), whether 1, 2, or 3 times its volume of the liquid be employed. Other varieties of wood-creosote are somewhat more soluble in glycerin, but the solutions are readily precipitated on adding water. Guaiacol dissolves in absolute glycerol, but is precipitated by dilution

d. Hager modifies this test by using somewhat diluted glycerin. 3 volumes of absolute glycerol mixed with 1 volume of water is an appropriate strength. For the detection of coal-tar acids in wood-creosote, 1 volume of the sample should be thoroughly agitated in a Mohr's burette with 3 volumes of the diluted glycerin, and the liquid allowed to stand till separation has occurred. If the creosote be pure, the volume will remain unchanged. If reduced, the glycerin layer is tapped off, and the remaining creosote again shaken with 3 times its volume of diluted glycerin and the volume again observed. This second treatment will always suffice for the removal of the coal-tar acids, unless their proportion is very large, and hence the volume of the residual layer will indicate the proportion of real wood creosote in the quantity of the sample taken. The nature of the residual creosote can be verified by the collodion test (*a*), while the coal-tar acids can be recovered from the glycerin solution by filtering it to remove suspended traces of wood creosote, diluting with water, and agitating with chloroform. On spontaneous evaporation of the separated chloroform, the coal-tar acids are obtained in a condition of sufficient purity to allow of their positive recognition.

Hager's modification of the glycerin test for creosote was examined in Allen's laboratory by W. Chattaway with fairly favourable results. The following figures, obtained with mixtures of wood creosote and Calvert's No. 5 carbolic acid, show the approximation to the truth of which the method is capable:

Taken		Found	
Wood-creosote	Coal-tar phenols	Residual layer	Recovered by chloroform
9 c.c.	1 c.c.	9.0 c.c.	0.96 grm.
8 c.c.	2 c.c.	8.0 c.c.	1.82 grm.
6 c.c.	4 c.c.	6.3 c.c.	3.46 grm.
4 c.c.	6 c.c.	4.0 c.c.	5.22 grm.

The portion left undissolved after the second treatment with dilute glycerin had all the characters of wood-creosote. It did not coagulate collodion. The portion dissolved by the glycerin and subsequently recovered by chloroform behaved like coal-tar acids with collodion and ferric chloride. Hence the separation by glycerin is fairly perfect.

From the foregoing reactions it will be seen that phenol, cresols, and wood-creosote can be readily distinguished from each other.

The case is different when a mixture of the substances has to be dealt with, as in the case of a sample of wood-creosote adulterated with crude carbolic acid. As the problem is to detect the coal-tar acids in presence of wood-creosote, rather than the reverse, only affirmative tests for the former substances are of service, and in many cases these are seriously modified by the simultaneous presence of creosote. In fact, the reactions with glycerin and collodion are the only 2 simple tests of real service, and these are much affected by the presence of a considerable proportion of wood creosote. If, however, the sample be treated with diluted glycerin, as described under *d*, and the ferric chloride and collodion tests be applied to the residue recovered by chloroform from the glycerin solution, the recognition of the coal-tar acids can be satisfactorily effected. These tests are best applied to the portion dissolved by the first treatment with glycerin, a second treatment being necessary to complete the extraction of the coal-tar acids, but the additional quantity dissolved is liable to contain sufficient creosote to obscure the blue coloration with ferric chloride. In employing these tests it must be remembered that genuine wood creosote contains distinct traces of phenol and cresols and still more of xylenols, and hence adulteration should not be assumed unless the treatment with diluted glycerin effects the removal of a very notable quantity of coal-tar acids.

A possible addition to wood-creosote, but one which does not appear to have been noted, is that of *blast-furnace creosote*. This, being of very similar composition to wood creosote, is very difficult to detect. The phenolic substances from blast-furnace creosote oils were distilled, and the fraction passing over between 210° and 220° examined in Allen's laboratory by the foregoing tests for wood creosote. The fraction itself readily gelatinised collodion, and gave with ferric chloride (test *b* 1) a slate-blue coloration changing to dirty brown. On treatment with diluted glycerin the greater part remained undissolved, but the dissolved portion when recovered by chloroform had the odour of common phenol, coagulated collodion, and reacted with ferric chloride almost exactly like Calvert's No. 5 carbolic acid, except that by test *b* 1 the violet-blue changed to brown instead of being permanent. These reactions would allow of the detection of blast-furnace creosote in wood creosote, but the insolubility of the greater part of the former product in diluted glycerin would render a separation of the two impossible by that means.

If the adulteration of wood-creosote by the portion of the blast-furnace product insoluble in glycerin were to be attempted, the reaction with ferric chloride and the gelatinisation of collodion would suffice to detect the substitution.

TRIHYDRIC PHENOLS

Of the trihydric phenols only two, viz, pyrogallol and phloroglucinol are important. These compounds are very similar in properties and reactions to the dihydric phenols.

Pyrogallol (1, 2, 3, trihydroxybenzene) is of importance as a photographic developer and as an absorbant for oxygen in gas analysis, etc. It is made by heating gallic acid alone or with water. It melts at 132° and sublimes to form white leaflets or needles. 100 grm. water at 25° dissolves 62.5 grm. pyrogallol. 100 grm. alcohol at 25° dissolves 100 grm. pyrogallol. Its alkaline solution has a powerful absorbent action for oxygen.

A solution of pyrogallol treated with lead acetate gives a white precipitate. Ferric chloride gives a red colour. Strong acetic acid and formaldehyde heated to boiling with pyrogallol gives no colour until treated with a few drops of hydrochloric acid, when a red colour is produced. A quantitative method of estimating pyrogallol has been based upon the violet coloration which it gives with a solution of ferrous sulphate and Rochelle salt, a colorimetric comparison being made with a standard solution of pyrogallol (Mitchell, *Analyst*, 1923, **48**, 1). A similar method has also been based on the violet coloration given by pyrogallol with osmium tetroxide (*Analyst*, 1924, **49**, 162).

Phloroglucinol (1, 3, 5 trihydroxybenzene) is made by fusing certain resins such as catechu, kino, etc. with caustic potash. It is also produced when resorcinol is fused with caustic soda. It melts at 218° and sublimes without decomposition. It crystallises with two molecules of water to form large colourless prisms. It is precipitated by lead acetate and gives a dark violet coloration with ferric chloride.

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AROMATIC ACIDS

BY EDWARD HORTON, B. Sc.

The true aromatic acids form a well-defined and important group of substances containing a benzene-nucleus. Many of them occur ready-formed, either free or combined, in resins, balsams and essential oils, as well as in animal organisms; many are prepared synthetically from constituents of coal-tar. The most important series of aromatic acids bears the same relation to benzene and its homologues as the aliphatic acids bear to methane and its homologues (paraffins), and the 2 series of acids present many points of resemblance. Just as acetic acid may be regarded as the type of a fatty or aliphatic acid, so benzoic acid is representative of the aromatic or cyclic acids; whilst a parallel to acrylic acid may be found in cinnamic acid, to glycollic and lactic acids in salicylic acid, to succinic acid in phthalic acid, and so on. The following tabular arrangement renders these analogies more evident:

Fatty (aliphatic) acids		Aromatic (cyclic) acids	
Formic	$H.COOH$	Benzoic (phenyl-formic)	$C_6H_5.COOH$
Acetic	$CH_3.COOH$	Toluic	$C_7H_7.COOH$
Propionic	$C_2H_5.COOH$	Xylic	$C_8H_9.COOH$
Acrylic	$C_2H_3.COOH$	Atropic (λ-phenyl-acrylic) Cinnamic (β-phenyl-acrylic)	$C_6H_5.C_2H_2.COOH$
Propiolic	$C_2H.COOH$	Phenyl-propiolic	$C_6H_5.C_2.COOH$
Glycollic	$CH_2(OH).COOH$	Salicyclic (hydroxybenzoic)	$C_6H_4(OH).COOH$
Glyoxylic	$CH(OH)_2.COOH$	Protocatechuic (dihydroxybenzoic)	$C_6H_3(OH)_2.COOH$
Erythric	$C_3H_4(OH)_3.COOH$	Gallic (trihydroxybenzoic)	$C_6H_2(OH)_3.COOH$
Succinic	$C_2H_4\!:\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$	Phthalic	$C_6H_4\!:\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.$

All, or nearly all, the aromatic acids in the foregoing table may be extracted by ether from their aqueous solutions. When heated with lime, they split up into carbon dioxide and benzene, hydroxybenzene, or homologues or analogues thereof. Thus:—

Phthalic acid............ $C_8H_6O_4 = CO_2 + C_7H_6O_2$, Benzoic acid.
Benzoic acid .... $C_7H_6O_2 = CO_2 + C_6H_6$, Benzene.
Toluic acid.............. $C_8H_8O_2 = CO_2 + C_7H_8$, Toluene.
Cinnamic acid.......... $C_9H_8O_2 = CO_2 + C_8H_8$, Cinnamene.
Salicylic acid........... $C_7H_6O_3 = CO_2 + C_6H_6O$, Phenol.
Cresotic acid .... $C_8H_8O_3 = CO_2 + C_7H_8O$, Cresol.
Protocatechuic acid..... $C_7H_6O_4 = CO_2 + C_6H_6O_2$, Catechol.
Gallic acid.............. $C_7H_6O_5 = CO_2 + C_6H_6O_3$, Pyrogallol.

In connection with the true aromatic acids, all of which contain 1 or more carboxyl-groups, CO.OH, the phenolsulphonic acids and certain allied compounds may be conveniently considered.[1] The chief aldehydes, salts, and esters of the aromatic acids are also described in this section, as also are related substances, such as saccharin and acetophenone. The various substances are classified under the following groups:

Sulphonated Phenols and their Allies.
Benzoic Acid and its Derivatives.
Cinnamic Acid and its Derivatives.
Salicylic Acid and its Allies.
Protocatechuic Acid and its Allies.
Gallic Acid and its Derivatives.
Phthalic Acids.

SULPHONATED PHENOLS AND THEIR ALLIES

By the action of concentrated sulphuric acid, phenol may be converted into compounds in which 1 or more of the hydrogen atoms of the benzene-nucleus are replaced by SO_3H groups. The *sulphonic acids* thus obtained usually form soluble barium salts, and hence may be separated from any sulphuric acid which has not entered into the reaction by treating the aqueous solution of the product with excess of barium carbonate and filtering.

The phenol-sulphonic acids may also be conveniently separated from the crude product by diluting this with water and saturating the liquid with common salt, when the sulphonic acids separate out as crystalline sodium salts, which may be purified by recrystallisation.

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[1] Except the sulphonic acids and quinolinic acid (which is a member of the heterocyclic group), all the acids described in this chapter are members of the true hexacarbocyclic series.

The homologues of phenol, the dihydroxy and trihydroxy phenols, and other analogous substances, also form sulphonic acids by treatment with concentrated sulphuric acid, the resultant compounds all being split up with formation of the original phenolic substances when heated with concentrated hydrochloric acid at a temperature between 100° and 200°. This general reaction is valuable, as the various isomerides and homologues may usually be separated with comparative facility by fractional crystallisation in the form of salts of their respective sulphonic acids, and the phenols then regenerated by treating these sulphonates with hydrochloric acid.

PHENOL SULPHONIC ACIDS

When phenol is treated with concentrated sulphuric acid it is converted into a mixture of sulphonic acids, the composition of which varies with the conditions (Kekulé, *Ber.*, 1869, **2**, 330; Engelhard and Latschinow, *Zeitsch. Chem.*, 1868, **4**, 77; Post, *Ber.*, 1875, **8**, 1547; Obermiller, *Ber.*, 1907, **40**, 3623). To obtain the ortho-acid the reaction is carried out at the ordinary temperature, but even under the most favourable conditions 3 parts of the para- are formed with every 2 parts of the ortho-acid, whilst a considerable amount of the phenol remains unattacked (Obermiller). By working at 100° to 110° the phenol-*o*-sulphonic acid is almost completely transformed into the para-isomeride. A small quantity of the meta-acid is also formed and, in the presence of a large excess of sulphuric acid, some phenol 2:4-disulphonic acid is produced.[1]

The ortho- and para-acids are most readily separated by the fractional crystallisation of their barium and magnesium salts. (Obermiller.)

The following table shows the characters of the 3 isomeric phenol-monosulphonic acids and some of their salts:

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[1] Similar series of substances, the cresol and xylenol-sulphonic acids, are obtained by the action of strong sulphuric acid on cresol (Claus and Kraus, *Ber.*, 1887, **20**, 3089; Hantke, *ibid.*, 3209) and xylenols, respectively. In the sulphonation of *m*-cresol, whatever the conditions, only one, *mono*-sulphonic acid is obtained. By employing a larger proportion of sulphuric acid a *di*-sulphonic acid is formed, and by heating the cresol to 180° with fuming sulphuric acid, a *tri*-sulphonic acid is produced. When *o*-cresol is heated with sulphuric acid to 100° only *o*-cresol-*p*-sulphonic acid is formed, but at the ordinary temperature *o*-cresol-*m*-sulphonic acid is also produced. When the concentrated aqueous solution of the latter acid is heated, it is converted into the former acid.

	Ortho-acid $C_6H_4 \left\{ \begin{matrix} OH_{(1)} \\ SO_3H_{(2)} \end{matrix} \right.$	Meta-acid $C_6H_4 \left\{ \begin{matrix} OH_{(1)} \\ SO_3H_{(3)} \end{matrix} \right.$	Para-acid $C_6H_4 \left\{ \begin{matrix} OH_{(1)} \\ SO_3H_{(4)} \end{matrix} \right.$
Free acid..........	At ordinary temperature, liquid; sp. gr. 1.400. Crystallises at 8° to 10°, and boils at 130°.	Crystallises in fine needles containing $2H_2O$.	Syrupy liquid; or hydrated, highly deliquescent needles.
Potassium salt......	Melts at 240°, resolidifying to a vitreous mass. Long, flat prisms containing 2 H_2O. Very soluble.	Melts at 200° to 210°. Confused efflorescent microscopic needles or scales containing $1H_2O$.	Melts at 400°. Anhydrous elongated hexagonal tables. Moderately soluble.
Sodium salt........	Indistinct crystalline masses containing 1½ H_2O.	Flat needles or rhombic tables containing $1H_2O$.	Long prisms containing $2H_2O$.
Barium salt........	Indistinct crystalline masses containing $2H_2O$. Very soluble.	Small laminæ of microscopic needles containing ½ H_2O. Easily soluble.	Long silky matted needles containing $3H_2O$.
Lead salt..........	Indistinct tables containing $1H_2O$. Very slightly soluble.	Large rhombic tables containing $3H_2O$.	Long bundles of needles containing $2H_2O$. Basic salt nearly insoluble.
Cupric salt.........	Pale blue prisms.	Thin bright green rhombic prisms containing $6H_2O$.	Deep blue plates, resembling cupric sulphate. Contains $10H_2O$.

The phenol-sulphonic acids are very stable substances and are not decomposed by boiling with alkali hydroxides.

By heating the free phenol-sulphonic acids or their salts with hydrochloric or dilute sulphuric acid under pressure, they are all decomposed completely with more or less facility, phenol being reproduced: $C_6H_4(OH)SO_3K + H_2O = C_6H_5.OH + KHSO_4$.

PHENOL-*o*-SULPHONIC ACID

This substance has been employed as an antiseptic under the names *aseptol*, *sozolic acid*, and *sulphocarbol*, but Obermiller (*loc. cit.*) states that aseptol, which is sold as a 33% aqueous solution of phenol-*o*-sulphonic acid, really consists of a solution of the impure para-acid containing about 6% of the ortho-acid.

When the potassium salt is heated with potassium hydroxide at 250° it yields catechol. Contrary to Kekulé's statement, Obermiller finds that phenol-*o*-sulphonic acid is not converted into the para-acid on boiling its aqueous solution. It has very little corrosive action, is practically non-poisonous, and is said to have an antiseptic action 3 times as powerful as that of phenol, whilst the sodium salt is still more energetic.

PHENOL-*m*-SULPHONIC ACID

A small quantity of this acid is stated by Obermiller to be formed in the direct sulphonation of phenol. In quantity it is prepared by heating benzene-*m*-disulphonic acid with aqueous potassium hydroxide solution at 170–180° (*Ber.*, 1876, **9**, 969).

When heated at 250° with potassium hydroxide phenol-*m*-sulphonic acid gives resorcinol.

PHENOL-*p*-SULPHONIC-ACID. SULPHOPHENIC ACID

This acid, known also commercially as sulphocarbolic acid, is a powerful antiseptic and its solutions coagulate albumin. By heating it at 250° with potassium hydroxide, phenol-*p*-sulphonic acid is converted not into quinol but into resorcinol. When oxidised with manganese dioxide and sulphuric acid it yields quinone.

Sodium phenol-p-sulphonate, $NaSO_3.C_6H_4.OH$, is prepared by double decomposition from the barium salt, and is the sodium sulphocarbolate of the Pharmacopœias.[1] It forms transparent rhombic crystals containing $2H_2O$, which are readily soluble in water, and have a cooling, saline, slightly bitter taste. The salt is permanent in the air, but becomes anhydrous at 100°. At a higher temperature it evolves phenol and leaves a residue of sodium sulphate and sulphite amounting to 30.6% of the weight of the crystallised salt.

Aluminium phenol-p-sulphonate, $Al[O.SO_2C_6H_4OH]_3$ may be prepared by double decomposition. It is very soluble in water, alcohol, and glycerol, and the solutions can be kept unchanged. The salt has been introduced under the name of "*Sozal*" as a material for antiseptic dressings.

Zinc phenol-p-sulphonate forms transparent efflorescent prisms or plates containing $7H_2O$ ($8H_2O$, United States Pharmacopœia, 9th Rev.). It also occurs as a white powder. It should leave 15.08% (14.6%, United States Pharmacopœia, 9th Rev.) of zinc oxide on strong ignition. The probable impurities are ***sulphates***, ***chlorides***, compounds of the ***light metals***, and free ***phenol***. If prepared by the British Pharmacopœia process, a notable quantity of sulphate is certain to be present.[2]

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[1] Sodium phenol sulphonate, United States Pharmacopœia, 9th Rev.

[2] The British Pharmacopœia of 1885 directed the salt to be prepared "by heating a mixture of carbolic acid and sulphuric acid, saturating the product with oxide of zinc, evaporating and crystallising." The solution of the product was stated to be "only rendered faintly turbid" by barium chloride. The description in the B. Pharmacopœia of 1898 is even more discreditable, for while omitting the words "evaporating and crystallising," it describes the product as giving "only the slightest reactions with the tests for sulphates." The salt is not included in the B. P. of 1914.

According to Andanti (*Boll. Chim. farm.*, 1917, **56**, 317–318), in the presence of an acid the phenolsulphonic radicle in zinc phenolsulphonate is completely converted by bromine into tribromophenol. The following method of estimating the sulphonate is based upon this fact. Exactly 0.5 grm. of the crystallised zinc phenolsulphonate is dissolved in water and the solution diluted to 500 c.c. In a stoppered flask of about 300 c.c. capacity, 50 c.c. of the sulphonate solution are mixed with 50 c.c. of a 0.6% solution of potassium bromide and 50 c.c. of a 0.1671% solution of potassium bromide. Five c.c. of concentrated sulphuric acid are then added, the flask shaken and left closed in a dark place at about 25° for three hours. Ten c.c. of a recently prepared 10% potassium iodide solution are next added and, after the lapse of an hour, the iodine liberated is estimated by titration with N/10 sodium thiosulphate solution. The number of cubic centimeters of the thiosulphate used is subtracted from that required in a blank test with 50 c.c. of the bromide and 50 c.c. of the bromate solutions alone; the remainder multiplied by 0.00447 gives the weight in grm. of crystallised zinc phenolsulphonate $(OH.C_6H_4SO_3)_2Zn, 7H_2O$ in the 50 c.c. of solution taken.

Reactions of the Phenolsulphonic Acids and Phenolsulphonates.—The salts of all 3 phenolsulphonic acids give a deep purple colour with ferric chloride solution. The colour is discharged by acids. The same reaction is observed with salicylic acid and its salts.

When a solution of phenol-*p*-sulphonic acid is boiled for some minutes with an equal volume of strong nitric acid and the solution neutralised with potassium hydroxide solution, a yellow colour due to the formation of potassium picrate, is produced. In this way 1 part of the acid can be detected in 50,000 parts of water. Phenol gives the same reaction.

Addition of bromine to a solution of phenol-*p*-sulphonic acid or one of its salts gives a precipitate of tribromophenol. Although phenol itself gives this reaction, the liberation of sulphuric acid from the sulphonic acid enables this to be detected in the presence of phenol.

The phenol-*p*-sulphonates may be recognised by the tests for phenol-*p*-sulphonic acid already described. The phenol-*p*-sulphonates of the alkalies, if ignited alone, or those of other metals, if ignited with sodium carbonate, leave a residue containing sulphate. This reaction, the formation of sulphate by treatment with bromine or boiling with nitric acid, and non-extraction by ether from acidified solutions are characters which distinguish the phenol-*p*-sulphonates from salicylates.

The presence of unconverted *phenol* in phenol-*p*-sulphonates may be detected by acidifying the solution with diluted sulphuric acid and agitating the liquid with ether or chloroform. The phenol left on spontaneous evaporation of the ether may be detected by its odour and by the yellow colour developed on warming with nitric acid and then neutralising with potassium hydroxide. A faint colour should be neglected, as it may be due to a trace of phenol-*p*-sulphonic acid dissolved by the ether.

The barium, calcium, and lead salts of phenolsulphonic acid are more or less soluble. Hence sulphuric acid and *sulphates* may be readily detected and estimated by addition of barium chloride to the original solution. *Barium* and *calcium* salts may be detected in phenolsulphonates by dilute sulphuric acid and ammonium oxalate, respectively.

Analysis.—The following rapid method of analysis has been described by Desvergnes (*Ann. chim. anal.*, 1920, **2**, 211–214). From 5 to 6 grm. of the sample are dissolved in water and the solution diluted to 200 c.c., care being taken that the mixture does not become heated. *Total sulphuric acid* (*T*). 10 c.c. of the solution are mixed with 25 c.c. of water and 25 c.c. of hydrochloric acid saturated with bromine, boiled for 15 minutes, diluted with 200 c.c. of water cooled, filtered, and the sulphuric acid in the filtrate estimated as barium sulphate. *Combined sulphuric acid.* 10 c.c. of the solution are titrated with N/2 sodium hydroxide solution, using methyl orange as indicator; this gives the free sulphuric acid plus one-half the combined sulphuric acid or S, hence the combined sulphuric acid = 2 (T – S). *Phenol.* 10 c.c. of the solution are heated at 50° in a closed vessel for 30 minutes with 100 c.c. of water, 50 c.c. of hydrochloric acid (sp. gr. 1.18), and 25 c.c. of standardised potassium bromate and bromide solution containing 4 grm. of bromate and 14 grm. of bromide per litre; the mixture is then cooled and the excess of bromine estimated iodometrically. The amount of free sulphuric acid present is calculated from the results obtained and the proportion of phenol to combined sulphuric acid gives the quantities of mono- and di-sulphonic acids.

Estimation.—The estimation of phenol-*p*-sulphonic acid may be based on the reaction with nitric acid, the sulphuric acid produced being precipitated and weighed as barium sulphate, and thence the weight of sulphonic acid calculated.

According to Hübener (*Chem. Zeit.*, 1908, **32**, 485) the reaction of bromine with phenolsulphonic acid is incomplete. But, by boiling the sulphonic acid with a saturated solution of bromine in hydrochloric acid, the sulphonic group is completely eliminated and may be estimated in the filtrate (the tribromophenol is removed by filtration) in the usual way.

Obermiller gives the following directions (*Ber.*, 1909, **42**, 4361). The phenolsulphonate (0.2 to 0.3 grm.), together with 0.6 to 1.0 grm. or barium chloride, is dissolved in 100 c.c. of water containing 10 c.c. of hydrochloric acid (sp. gr. 1.19). The liquid is heated to between 60° and 65° and slowly treated with a solution containing 1 grm. of potassium bromate and 5 grm. of the bromide per 100 c.c., until a faint persistent yellow colour is produced. A small quantity of an alcoholic solution of phenol is added to remove the excess of bromine, and then sufficient alcohol to dissolve the tribromophenol. The liquid is boiled and decanted whilst hot from the barium sulphate, which is repeatedly washed by decantation with 59% alcohol, and then with water. It is finally filtered and weighed.

The following volumetric method is described by Smith and Frey (*J. Amer. Chem. Soc.*, 1912, **34**, 1040). A quantity of the sample corresponding with 0.18–0.20 grm. of phenol-*p*-sulphonic acid is dissolved in 50 c.c. of water in a stoppered long-necked 250 c.c. flask. To this are added 50 c.c. of an aqueous solution containing 2.7833 grm. of potassium bromate and about 40 grm. of potassium bromide per litre. 5 c.c. of hydrochloric acid (sp. gr. 1.18) are then added, the flask stoppered to prevent loss of bromine and the mixture kept at 20°–25° for not less than 10 and not more than 15 minutes, during which time no turbidity should be produced. Dibromophenolsulphonic acid is formed by the action of the free bromine, the excess of which is determined by titration with standard thiosulphate solution after the addition of potassium iodide. The method is accurate to ± 0.5%.

PHENOLPOLYSULPHONIC ACIDS

By digesting phenol at 100° with a considerable excess of fuming sulphuric acid, phenol 2:4-disulphonic acid is produced, whilst phenol 2:4:6-trisulphonic acid is formed when phenol is heated under pressure with sulphuric acid and phosphorus pentoxide.

The polysulphonic acids give a deep red colour with ferric chloride solution.

Phenol 2:4-disulphonic acid is employed in Grandval and Lajoux's method (*Compt. rend.*, 1885, **101**, 62) of estimating nitrates in water. (Compare also Gill, *Tech. Quarterly*, 1894, **7**, 55.)

A sodium mercuric phenol, 2:4-disulphonate, said to have the constitution $C_6H_3(OHg)\ (SO_3Na)_2$, is used under the name *Hermophenyl* as an internal antiseptic.[1]

IODOPHENOL-*p*-SULPHONIC ACIDS

When 1 molecule of iodine (in the form of a mixture of potassium iodate and iodide) is added gradually to 1 molecule of potassium phenol-*p*-sulphonate dissolved in excess of dilute hydrochloric acid, iodine at first separates, but is quickly reabsorbed, and after a short time the liquid sets to a dense mass of long thin prisms of *potassium 2:6:-diiodo-phenol-4-sulphonate*, $C_6H_2I_2(OH).SO_3K + 2H_2O$. This salt requires about 50 parts of water for solution, and when heated decomposes without melting at about 270°, with evolution of violet vapours of iodine. It yields with potassium hydroxide an extremely soluble basic salt, $C_6H_2I_2(OK).SO_3K$. The *sodium salt* (normal) forms a white crystalline powder containing $2H_2O$, and is infusible at 200°. It is odourless, has a faintly acid taste, is soluble in 13 parts of cold water and more readily in hot, and is also soluble in alcohol. The magnesium, aluminium, zinc, and lead salts are readily soluble in water and glycerol, but the silver and mercury salts are but slightly soluble. The *barium salt* is only slightly soluble in cold water, from which it crystallises in white glistening needles. The *zinc salt* forms long colourless needles, and the *copper salt* pale green monoclinic prisms.

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[1] *Cosaprine* is the sodium salt of the sulphonic acid of acetanilide. It has the constitution $C_6H_4(NH.CO.CH_3)(^1)SO_3Na)(_4)$ and may be regarded as sodium phenol-*p*-sulphonate in which the hydroxyl-group has been replaced by an acetamino-group. It is an odourless, white, amorphous powder, of saline taste. It is a strong antipyretic, and presents the practical advantage of being readily soluble in water. Its solution should give no precipitate with barium chloride.

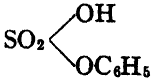
2:6-Diiodo-phenol-4-sulphonic acid is prepared commercially in the free state by treating diiodobenzene with fuming sulphuric acid, saturating the diluted liquid with lead carbonate, filtering, and decomposing the soluble lead salt by hydrogen sulphide. On concentrating the filtered liquid, the acid is deposited in crystals which melt at 120° and decompose at 190° with liberation of iodine.[1]

Diiodophenolsulphonic acid ($+3H_2O$) contains 52.9% of iodine, is odourless, and is a useful substitute for iodoform. Both the free acid and its salts possess well-marked antiseptic properties and are employed in medicine under the name of "*Soziodol.*" "Easily soluble soziodol" is the sodium salt, and is commonly given in solution, whilst the potassium salt forms the "difficulty soluble" modification (*Pharm. J.*, 1888, [iii], **18**, 538, 621, 1006). The potassium and zinc salts are used in ointments. The mercury salt has been employed as a hypodermic injection in cases of syphilis.

The following simple method of estimating mercury in *Hydrargyrum sozoiodolicum* has been described by Hermann (*Arch. Pharm.*, 1916, 254, 498–500). 0.5 grm. of the preparation is shaken with about 10 c.c. of water in a 200 c.c. glass-stoppered bottle, treated with 2 grm. of potassium iodide and, after the liberated mercuric iodide has dissolved, treated with 10 c.c. of officinal alkali hydroxide solution. A mixture of 3 c.c. of formaldehyde solution and about 10 c.c. of water is added and the bottle is gently shaken for about one minute. After acidifying with 25 c.c. of dilute acetic acid, 25 c.c. of N/10 iodine solution are added; and the excess of iodine is titrated with N/10 thiosulphate after all the mercury has been dissolved (1 c.c. of N/10 iodine solution = 0.010003 grm. of mercury = 0.031225 grm. of the mercuric salt).

PHENYLSULPHURIC ACID. PHENYL HYDROGEN SULPHATE

$C_6H_6SO_4$; *i. e.*, $(C_6H_5)HSO_4$; or



$$SO_2\begin{cases} OH \\ OC_6H_5 \end{cases}$$

This acid is isomeric with the phenol-monosulphonic acids, $C_6H_4(OH)SO_3H$. It occurs, together with its homologue cresyl-sulphuric acid, $(C_7H_7)HSO_4$, as a potassium salt in the urine of the horse and other herbivora. These salts also occur in considerable quantity in human urine after taking carbolic acid, and traces are normally present. During exhibition of phenol the inorganic sulphates ordinarily present in urine are greatly reduced in amount or even wholly disappear, being converted into phenyl-sulphates. The quantity of sulphur existing in normal human urine in the form of phenolic and other ethereal sulphates averages one-tenth of that present as metallic sulphates. The ethereal sulphates are represented by the potassium salts of phenyl-sulphuric acid, indoxyl-sulphuric acid, skatoxyl-sulphuric acid[1] and similar compounds of catechol and quinol. E. Baumann (*Ber.*, 1876, **9**, 55) has shown that if the inorganic sulphates be first precipitated by acidifying the urine with acetic acid and warming the diluted liquid with excess of barium chloride, the filtered liquid will contain any cresyl-sulphates and phenyl-sulphates which may be present. On strongly acidifying the filtrate with hydrochloric acid and boiling it for 1 hour the phenolic sulphates will be decomposed, barium sulphate being precipitated together with resinous matter, from which impurity it may be freed by washing with hot alcohol.[2] On subsequently distilling the acidified urine the distillate contains distinct traces of phenol, directly recognisable by the bromine test (see p. 279), and if the distillate be shaken with ether and the ethereal solution separated and cautiously evaporated, the residue gives a distinct blue colouration with ferric chloride. On the contrary, from the original urine no phenol can be extracted by agitation with ether, a behaviour evidently due to the fact that the phenyl-sulphates are not decomposed till the urine is heated with acid.[3]

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[1] In preparing the diiodo-acid, a certain amount of mono-iodophenolsulphonic acid is produced. This substance forms thick, colourless, rhombic crystals, and yields barium and calcium salts which are readily soluble in water.

Baumann (*loc. cit.*) has actually isolated potassium phenyl-sulphate from horses' urine by the following process: The liquid is evaporated at a low temperature, the residue extracted with alcohol, and the filtered liquid concentrated to a syrup and allowed to stand in a very cold place. The crystalline plates which form are filtered off, dried, and purified by recrystallisation from strong spirit. The pearly-white tables obtained consist of potassium phenyl-sulphate. L. Brieger treats fresh urine with neutral acetate of lead in excess, filters, and treats the filtrate with basic lead acetate. The lead is removed from the filtered liquid by hydrogen sulphide, and the filtrate evaporated to a thick syrup and kept for some time in a vacuum. The potassium phenyl-sulphate forms plates which are recrystallised from hot absolute alcohol (*Zeit. physiol. Chem.*, 1884 [iv], **8**, 311).

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[1] These compounds are fully described in Vol. VII.

[2] If the filtrate be evaporated to dryness, and the residue fused with nitre, an additional quantity of sulphuric acid is formed corresponding, in human urine, to 10–20 % of the total sulphur excreted, but rising in anomalous cases to a larger proportion. The unoxidised sulphur exists in the urine partly in the form of cystin, a substance having the composition $C\ H_{12}N_2S_2O_4$; but a portion is excreted in the form of thiocyanates.

[3] E. Davies has described a specimen of urine passed by a person recovering from poisoning by carbolic acid (*Pharm. J.*, 1883, (iii), 14, 473). It was almost black in colour, and on distillation with sulphuric acid gave a distillate containing both phenol and cresol. The phenol was recognised by the odour, the reaction with ammonia and sodium hypochlorite, and the formation of an abundant precipitate of tribromophenol (of characteristic crystalline form) and (tri) bromocresol on adding bromine. Only a trace of phenol distilled over when the addition of sulphuric acid was omitted, and no phenol could be extracted by ether.

Potassium Phenyl-sulphate, $(C_6H_5)KSO_4$, may also be prepared by the action of potassium phenoxide on potassium pyrosulphate: $(C_6H_5)OK + K_2S_2O_7 = K_2SO_4 + (C_6H_5)KSO_4$. It crystallises in transparent rhombic tablets which feel greasy to the touch. It is readily soluble in water and sparingly soluble in cold absolute alcohol, but dissolves somewhat more readily in boiling alcohol. The aqueous solution exhibits a fine blue fluorescence.

Potassium phenyl-sulphate decomposes on exposure to moist air, sometimes in a few minutes, into phenol and potassium hydrogen sulphate. A similar change occurs by boiling the aqueous solution for a few hours or warming it for a few minutes with dilute hydrochloric acid, but it is not affected by acetic acid. On the other hand, potassium phenyl-sulphate is stable in the presence of alkalies, and is only gradually attacked by potassium hydroxide at 150°. When the solid salt is heated to 150°–160° in absence of moisture it is converted into the isomeric potassium phenol-*p*-sulphonate.

Phenyl-sulphates are readily distinguished from phenol-sulphonates by the formation of phenol and a sulphate on heating the solution with hydrochloric acid. When solid potassium phenyl-sulphate is quickly heated to fusion, and then dissolved in water, the solution gives a ruby-red colour with ferric chloride.

Free phenyl-sulphuric acid is so unstable that its aqueous or alcoholic solution decomposes almost immediately. It has never been isolated.

NAPHTHOL SULPHONIC ACIDS

The practical application of the various acids obtained by the sulphonation of α- and β-naphthol is chiefly confined to the production of colouring-matters. Hence their preparation and characters are described in Vol. VI.

Asaprol or Abrastol is calcium β-naphthol-α-sulphonate, $[C_{10}H_6(OH)(SO_3)]_2Ca + 3H_2O$. It forms an odourless, crystalline, bitter powder, neutral in reaction, and soluble in water and alcohol, but not in ether. Asaprol is non-toxic, and is recommended (in doses of 4 grm.) as an antithermic in typhoid fever and articular rheumatism. It is also used as a clarifier and antiseptic in wines (see also p. 236).

Qualitative Tests and Detection.—The following reactions are described by Vitali (*Boll. chim. farm.*, 1908, **47**, 291). Abrastol gives a red colour with mercuric nitrate, a fine green fluorescence when treated with sulphuric acid and formaldehyde, a blue colour with Froehde's reagent, and a green tint with the vanadium-sulphuric acid reagent, all of which reactions can be observed with 0.0001 grm. of the substance. A solution of abrastol (0.1%) gives a blue colour with ferric chloride solution, a green colour with a blue fluorescence when chlorine water and a little ammonia are added, and an intense red colour changing to violet when the residue from the evaporation of 1 c.c. is treated with potassium nitrate solution and excess of sulphuric acid. Potassium nitrate solution gives a yellow colour which changes to green on evaporation and to blood-red on adding sulphuric acid. When evaporated to dryness with mercurous nitrate solution 1 c.c. of a 0.01% solution of abrastol leaves a residue having a fine violet-red colour. Abrastol gives a yellow colour with sulphuric acid and, in very dilute solution, a fine blue fluorescence with alkalies.

According to Salomone (*Giorn. Farm., Chim.* 1906, **55**, 481) a solution of abrastol, when treated with red fuming nitric acid, gives a ruby-red coloration not extracted by ether or chloroform. After some hours, or immediately on adding alkali, the colour changes to yellow. With a solution containing only 1 part of abrastol in 300,000 of water the reaction appears after a few minutes, especially if the liquid is warmed at 40° to 50°. If a small crystal of sodium hyposulphite is added the red colour changes to blue, violet, dark-green, and finally yellow, whilst with a crystal of sodium sulphite it changes immediately to yellow. Addition of stannous chloride solution, followed by a few drops of hydrogen peroxide or ammonium persulphate solution, changes the ruby-red colour to a reddish-violet which is intensified by adding sulphuric acid.

To detect abrastol in wines, Salomone extracts 25 to 50 c.c. of the sample with 15 to 30 c.c. of amyl alcohol containing a little ammonia, evaporates the extract, and tests the residue as above. Or the residue may be fused with sodium, the product dissolved in water, and the solution tested for alkali sulphide with sodium nitroprusside (distinction from naphthol).

To detect asaprol or abrastol in red wine, A. Sanna Pintus (*Staz. sper. agrar. ital.*, 1900, **33**, 274) shakes 10 c.c. of the cold sample with 2 grm. of animal charcoal, and adds to the filtered liquid an equal volume of a solution of mercuric nitrate containing nitrous acid (prepared by dissolving 10 grm. of mercury in 9.7 c.c. of nitric acid of 1.42 sp. gr. and adding 3.5 c.c. of water to the solution). In the presence of abrastol, an immediate yellow coloration, with a golden fluorescence, is produced, the colour changing to rose on exposure to the air for a few minutes. In the case of white wines the preliminary treatment with animal charcoal is unnecessary, and the test in that case is capable of detecting 0.01% of the antiseptic. (See page 236.)

Gabutti (*Staz. sper. agrar. ital.*, 1904, **37**, 234) states that 0.1 grm. of abrastol in 1 litre of wine can be detected by extracting 100 c.c., previously made alkaline with a few drops of ammonia, with 10 to 15 c.c. of amyl alcohol, filtering and evaporating the alcoholic extract, dissolving the residue in phosphoric acid (sp. gr. 1.7), heating with a few drops of concentrated formaldehyde solution, and filtering. In the presence of abrastol, the filtrate shows a green fluorescence.

According to Carletti (*Boll. chim. farm.*, 1909, **48**, 223) when a solution of as little as 0.00005 grm. of abrastol in concentrated sulphuric acid is treated with a few drops of a 10% aqueous or alcoholic solution of tartaric acid and gently warmed, an emerald-green coloration is produced. This reaction has the advantage over that with ferric chloride of being unaffected by organic acids.

Other methods of detection are described by Sanglé-Ferrière (*Compt. rend.*, 1893, **117**, 796), Sinabaldi (*Monit. Scient.*, 1893, **7**, 842), and Briand (*Compt. rend.*, 1894., **118**, 925). (See p. 236.)

HYDROXYQUINOLINE SULPHONIC ACIDS

Several sulphonated compounds derived from quinoline have been recently recommended as internal antiseptics. The following are the more important of these preparations:

Diaphtol or Quinaseptol,	$C_9H_5N(OH)(SO_3H)$.
Diaphterine or Oxyquinaseptol,	$(C_9H_6N.OH)_2.C_6H_4.OH.SO_3H$.
Hydrargyraseptol,	$C_9H_5N(OH)SO_3Hg + 2NaCl$.
Loretine,	$C_9H_4IN(OH)SO_3H$.

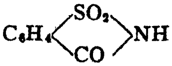
Diaphtol is hydroxyquinoline-3-sulphonic acid, diaphterine is a compound of 2-hydroxyquinoline (2 mols.) with phenol-*o*-sulphonic acid (1 mol.), while the last of the above compounds is a 3-iodo-2-hydroxy-quinoline sulphonic acid. It forms an odourless, yellow powder, insoluble in water and only slightly soluble in alcohol, ether, or oils. The sodium salt, known as "*soluble loretine*," dissolves in water with orange coloration. Both this compound and the free acid are powerful antiseptics used in surgery.

BENZOIC ACID AND ITS DERIVATIVES

Benzoic acid is the central member of a group of highly interesting compounds, a considerable number of which possess more or less practical interest. They all contain the radical *benzoyl*, C_7H_6O = $C_6H_5.CO$ = Bz, either intact or substituted.[1] In the following compounds the benzoyl radical exists intact:

Benzoic acid (phenyl-formic acid)	$C_6H_5.CO.OH$
Benzoyl chloride (benzoic chloride)	$C_6H_5.CO.Cl$
Benzoyl hydride (benzaldehyde)	$C_6H_5.CO.H$
Benzoyl methide (acetophenone)	$C_6H_5.CO.CH_3$
Benzoyl-glycocoll (hippuric acid)	$C_6H_5.CO.NH.CH_2.CO.OH$
Benzoyl-ecgonine	$C_6H_5.CO.C_9H_{14}NO_3$
Benzoyl-methylecgonine (cocaine)	$C_6H_6.CO.C_9H_{13}(CH_3)NO_3$
Benzoyl-acetyl-aconine (aconitine)	$C_6H_5.CO.(C_2H_3O)C_{25}H_{39}NO_9$

In the following allies of benzoic acid substitution occurs in the benzoyl radical itself:

Methylbenzoic acids (toluic acids)	$C_6H_4(CH_3).CO.OH$
Hydroxybenzoic acids (salicylic acid, etc.)	$C_6H_4(OH).CO.OH$
Dihydroxybenzoic acids (protocatechuic acid)	$C_6H_3(OH)_2.CO.OH$
Trihydroxybenzoic acids (gallic acid, etc.)	$C_6H_2(OH)_3.CO.OH$
Carboxylbenzoic acids (phthalic acids)	$C_6H_4CO.OH.CO.OH$
Nitrobenzoic acids	$C_6H_4(NO_2).CO.OH$
Aminobenzoic acids	$C_6H_4(NH_2).CO.OH$
Sulphobenzoic acids	$C_6H_4(SO_3H).CO.OH$
Sulphaminobenzoic acids	$C_6H_4(SO_2NH_2).CO.OH$
Sulphaminobenzoic anhydride (saccharin)	 $C_6H_4\langle{}^{SO_2}_{CO}\rangle NH$

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[1] A colour reaction for the detection of the benzoyl group in organic compounds has been described by G. Denigès (*Analyst*, 1899, 24, 268). The indications are of very doubtful value.

Many of these substituted benzoic acids have received important applications and are described in detail in the sequel.

BENZOIC ACID

Benzene-carboxylic Acid. Phenyl-formic Acid

$C_7H_6O_2$; or, $C_6H_5.COOH$

Benzoic acid occurs ready-formed in gum benzoin, storax, and Tolu and Peruvian balsams, and in these and other resins also in the form of benzoic esters. It has also been found in the perfume known as *ylang-ylang*, in vanilla, in oil of jasmine, and in certain fruits, notably plums and cranberries.

Benzoic acid is formed in numerous synthetic reactions, and is produced by the oxidation of a great number of organic substances, including benzoic and cinnamic aldehydes, toluene, cumene, casein, gelatin, etc.

From gum benzoin the benzoic acid may be obtained by sublimation, or by exhaustion of the powdered substance with carbon disulphide. It may also be extracted from benzoin by treatment with lime in the manner indicated on page 453. Benzoic acid prepared from gum-benzoin by sublimation is often more or less coloured, and has an aromatic odour.

It is prepared commercially by oxidising benzyl chloride with nitric acid.

Benzoic acid crystallises from hot water in white lustrous scales or friable needles, but its crystalline habit is greatly modified by traces of impurity, so that the impure substance has been several times mistaken for an isomeric acid. When quite pure, benzoic acid is almost, if not quite, odourless,[1] but as met with in commerce it always has a well-marked odour, frequently smelling of benzoin, and sometimes of urine or almonds.

Benzoic acid has a sp. gr. of 1.292, melts at 121°, and boils at 249°. It volatilises readily at a temperature much below its b. p., forming a beautiful feathery sublimate. The acid is somewhat volatile in a current of steam, and more or less with alcohol, benzene, and other volatile liquids.

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[1] 4 specimens of benzoic acid prepared by different methods and carefully purified were found by Perry to lose odour as the purification proceeded, becoming quite odourless when strictly pure. The merest trace of benzyl alcohol, benzyl benzoate, or benzaldehyde imparted a marked odour to the acid.

Benzoic acid has a sharp taste, and produces a peculiar irritation in the throat. The vapour has a penetrating aromatic odour, attacks the eyes, and provokes coughing.

In cold water benzoic acid dissolves very sparingly, requiring 640 parts at 0°, 408 at 15° and 281 at 25°.[1] In boiling water the solubility is 1 in 17 (1 in 15, United States Pharmacopœia). Benzoic acid is dissolved very readily by alcohol, ether, chloroform, amyl alcohol, benzene, petroleum spirit, carbon disulphide, and some fixed and volatile oils.

Benzoic acid is employed in medicine and in the manufacture of colouring-matters. It possesses decided antiseptic properties, being in this respect, according to some observers, superior to salicylic acid, and, according to others, inferior.

In the report of an investigation into the effects on digestion and health, of the presence of benzoic acid or sodium benzoate in foodstuffs, H. W. Wiley (*U. S. Dept., Agric. Bureau. Chem.*, Circular No. 39, 1908) states that both these substances are highly objectionable when taken internally, the evil effects being manifested by indigestion, nausea, headache, vomiting, loss of body-weight, etc. The importance of detecting any addition of benzoic acid to foods is therefore evident.

The Referee Board appointed by the President of the United States carried out 3 independent tests during a period of 3 months and reported that benzoic acid and benzoates in moderate doses, such as would be used in foods, were harmless and that there was no cumulative effect.

Commercial Benzoic Acid.—The benzoic acid of commerce is liable to contain various impurities, some of which are due to its mode of preparation, whilst others are intentionally added as adulterants. Asbestos, boric acid, calcium carbonate and sulphate, sal-ammoniac, and sugar are among the more or less apocryphal additions of the latter class.

Pure benzoic acid does not melt in boiling water, but some impurities impart this property to it, besides giving it greater solubility, and causing it to form smaller crystals of a different form from that usually assumed by the pure acid. On treating a sample of benzoic acid with ether, nearly all impurities and adulterants are left undissolved, except cinnamic acid, chlorobenzoic acid, and essential oil.

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[1] The solubility of benzoic acid in water is much increased by the presence of certain salts, such as sodium phosphate.

Sodium Benzene-sulphinate is a compound obtained by dissolving benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature and the solution has been recommended as an antiseptic dressing for wounds. It is said to be more efficient than phenol, and to rank with mercuric salts and iodoform, without having the poisonous characters of the former or the disagreeable odour of the latter.

Inorganic impurities in benzoic acid can be detected and estimated by subliming the sample, pure benzoic acid being readily and entirely volatile. If the residue chars on further heating, *sugar* or *hippuric acid* may be present. The former gives a smell resembling burnt bread, and the latter an odour of burnt feathers, and they may be readily distinguished in other ways. *Boric acid* is insoluble in ether, but dissolves in hot alcohol to form a solution which when kindled burns with a flame green at the edges. If this indication be obtained it should be confirmed by repetition on the residue left on dissolving the sample in ether, as chlorobenzoic acid might also give rise to a green-edged flame.

Hippuric acid when present may be further detected by its incomplete solubility in ether; by its charring when heated with strong sulphuric acid; and by the evolution of ammonia which occurs when the sample is ignited with soda-lime. The last test may be employed quantitatively in the absence of ammoniacal salts. The proportion of hippuric acid may be approximately estimated by agitating the sample with dilute hydrochloric acid and petroleum spirit or chloroform, when any hippuric (or succinic) acid remains undissolved. Samples of benzoic acid containing hippuric acid usually have a urinous odour, and redden or char when heated.

Salicylic acid may be detected by the production of a violet coloration with excess of ferric chloride. It may also be detected and estimated by treating the warm aqueous solution of the sample with bromine water which throws down the salicylic acid completely as a white, voluminous precipitate, whilst benzoic acid gives no reaction. (Compare page 486.)

Cinnamic acid is said to be often present in considerable proportion in benzoic acid prepared from benzoin. It is best detected by its reaction with manganous salts (see page 432), and by the smell of bitter-almond oil produced on warming the sample with sulphuric acid and potassium dichromate. The presence of cinnamic acid lowers the m. p. of benzoic acid.

According to A. Jorissen (*Ann. chim. anal.*, 1901, **6**, 41), cinnamic acid can be detected in benzoic acid in the following way: 1 grm. of the sample is dissolved in 10 c.c. of boiling water, and the solution cooled and filtered. The crystals on the filter are gently pressed to expel the mother-liquor. The latter is transferred to a test-tube, treated with 4 c.c. of a 5% aqueous solution of uranium acetate, the tube closed with a cork, and the liquid exposed to light, direct sunlight if possible. In the presence of cinnamic acid, of which 1% can be thus detected, benzaldehyde is gradually formed and can be recognised by its odour.

Chlorinated compounds are indicative of the presence of synthetic benzoic acid and should never be present in an acid prepared from natural sources. They may be detected by dissolving the sample in alcohol, moistening some asbestos with the solution, igniting it, and placing a beaker moistened with silver nitrate over the flame. If chlorinated products were present, a milky deposit of silver chloride will be produced. P. N. Raikow (*Chem. Zeit.*, 1898, **22**, 20) states that if a portion of the sample be heated on a platinum wire over a bunsen flame, and the evolved vapours allowed to come into contact with a few drops of an alcoholic solution of phloroglucinol-vanillin contained in an inverted porcelain dish held over the flame, a red colour will be developed in presence of organic chlorinated compounds.

For the detection of halogens in the benzoic acid of commerce, Wende (*Apoth. Zeit.*, 1914, **29**, 157) gives the following test: A mixture of 0.1 grm. of the sample with 0.5 grm. of yellow mercuric oxide is heated in a dry test-tube, the latter being constantly turned over a flame about 1 cm. high. When the action is over, about 10 c.c. of dilute nitric acid are added, the whole heated nearly to boiling and filtered. The filtrate should not give more than a slight opalescence with silver nitrate solution.

The British Pharmacopœia 1914 requires benzoic acid to conform to the following standard:

> "When 0.5 grm. is heated in a closed crucible with twice its weight of calcium carbonate, the mass dissolved in diluted nitric acid, and solution of silver nitrate added, not more than the slightest cloudiness results (absence of chlorobenzoic acid). Yields no characteristic reactions for oxalates. Does not develop the odour of benzaldehyde when warmed with its own weight of potassium permanganate and 10 times its weight of dilute sulphuric acid (absence of cinnamic acid). Arsenic limit 2 parts per million."

According to the standard set by the U. S. Pharmacopœia benzoic acid must not contain more than 0.05% of ash, must give no odour of benzaldehyde when 0.5 grm. of the acid is heated at 45° for 10 minutes with 0.5 grm. of potassium permanganate and 5 c.c. of water (absence of cinnamic acid) and must contain not less than 99.5% of $C_7H_6O_2$ when titrated in dilute alcoholic solution with N/10 potassium hydroxide solution using phenolphthalein as indicator. Further the chlorides and "easily carbonisable impurities" must not exceed those shown in the following tests.

"A solution of about 0.1 grm. of synthetic benzoic acid in 2 c.c. of sulphuric acid does not become darker than light yellow when warmed for 5 minutes at 50°. The colour produced by the acid from benzoin tested in the same manner does not become darker than light brown. Mix 0.5 grm. of the acid and about 1 grm. of calcium carbonate (free from chloride) with a little distilled water in a crucible, dry the mixture and incinerate at a low red heat. Dissolve the residue in 2.5 c.c. of diluted nitric acid (free from chloride) and filter. If the synthetic acid is being tested, the addition of 0.5 c.c. of silver nitrate solution to the filtrate does not produce a greater turbidity than is produced by the same quantity of reagent in a mixture of 25 c.c. of distilled water and 0.1 c.c. of N/10 hydrochloric acid solution. If the acid from benzoin is being tested, the turbidity is not greater than that produced by the same quantity of reagent in a mixture of 25 c.c. of distilled water and 0.05 c.c. of N/10 hydrochloric acid solution."

Traces of *hydrochloric* and *sulphuric acids* are frequently present in commercial benzoic acid, owing to the method of preparation.

Sugar is recognised by its insolubility in ether, ready solubility in cold water, and by the blackening which occurs when the sample is heated with strong sulphuric acid. When present in quantity it may be detected by the taste of the sample, and in smaller quantity by the taste of the residue left undissolved by ether or chloroform.

Ammonium chloride (sal-ammoniac) is detected by shaking the sample with cold water, when a solution is obtained with which silver nitrate gives white curdy silver chloride insoluble in nitric acid. This proves the presence of a chloride only; the presumption that ammonium chloride is present is confirmed if the sample evolves ammonia on treatment *in the cold* with alkali hydroxide. In presence of ammonium chloride and other ammoniacal salts, the soda-lime test for hippuric acid is inapplicable, unless the sample be first shaken with cold, moderately concentrated hydrochloric acid, in which ammonium chloride dissolves, whilst hippuric acid is nearly insoluble.

Essential oil, which is very commonly present in benzoic acid made from gum benzoin, causes the samples to turn brown when warmed with strong sulphuric acid. *Resinous* and *oily matters* will remain undissolved, together with any mineral matters, on treating the sample with sufficient warm dilute sodium hydroxide solution to neutralise the acid.

The odour of benzoic acid to some extent indicates its origin; but the acid from benzoin is sometimes imitated by mixing the products from other sources with benzoin, and subliming the mixture; or by adding vanillin to artificial benzoic acid. According to Hager, (*Pharm. Central.*, 1886, **26**, 392), this factitious product may be detected by a mixture of solutions of ferric chloride and potassium ferricyanide. With the natural acid from benzoin, the colour of this reagent is changed from yellow to blue in from 1 to 3 seconds; whilst with the product obtained by subliming the artificial acid over resin, from 20 seconds to 2 minutes are required. The pure acid does not change the colour.

The reduction of potassium permanganate has been proposed as a test for the origin of benzoic acid, but its indications have been proved to be fallacious. Ammonio-nitrate of silver has also been recommended, the test being used at a boiling heat.

O. Jacobsen (*Arch. Pharm.*, 1884, [iii], **22**, 366) recognises the acid from gum benzoin by the presence of *catechol*, which he detects by converting the acid into a sodium salt, drying, and shaking with ether. The ether being separated and evaporated, the residue is dissolved and the catechol recognised by its reducing action on cold ammonionitrate of silver and by other reactions.

Jacobsen has further investigated the nature of the substances accompanying benzoic acid prepared from gum benzoin. On treating such acid with a solution of sodium carbonate, an oil remains undissolved, smelling of vanillin and of phenol. This may be separated by distillation into 3 fractions. The first, boiling between 200° and 210°, consists of methyl benzoate and guaiacol, which can be separated by cold dilute sodium hydroxide solution. The second and smaller fraction (boiling between 235° and 245°) when shaken with water yields catechol, whilst acetyl-guaiacol remains undissolved. The third and largest fraction (boiling between 280° and 330°) contains benzyl benzoate, benzophenone, and benzoyl-guaiacol, with traces of vanillin and other substances. On saponification with alcoholic potassium hydroxide, and agitation with water and ether, benzyl alcohol and benzophenone pass into the ethereal layer, whilst the alkaline solution contains benzoic acid and guaiacol. The 2 latter substances may be separated by adding sodium hydrogen carbonate till the liquid is alkaline to litmus, and then agitating with ether, which will dissolve the guaiacol only.

Pure benzoic acid, when heated in a test-tube, sublimes completely without changing colour. It dissolves to a colourless solution in pure sulphuric acid, and if ignited with calcium carbonate, leaves a residue, the solution of which, in nitric acid, gives no opalescence with silver nitrate solution. Consequently, a sample which satisfies these 3 tests can contain no likely impurity, except salicylic and sulphuric acids, which can be detected as above.

Qualitative Tests and Detection.—Strong solutions of soluble benzoates are precipitated on addition of hydrochloric acid, owing to the slight solubility of benzoic acid in water. (Succinates give no precipitate with hydrochloric acid; but hippurates, cinnamates, and salicylates react like benzoates. Sulphuric acid should not be substituted for hydrochloric acid.)

Sodium amalgam, metallic magnesium, or aluminium gradually reduce a slightly acidified solution of a benzoate, with production of the characteristic odour of benzaldehyde.

Neutral ferric chloride precipitates neutral benzoates almost completely as a light red, bulky, basic ferric benzoate, insoluble in acetic acid. Succinates give with ferric chloride a reddish-brown, cinnamates a yellow, and hippurates a cream-coloured precipitate, meconates a deep red coloration, and salicylates a violet coloration. Benzoic acid is also distinguished from succinic and many other acids by not being precipitated by ammoniacal barium chloride in presence of alcohol. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

For the detection of benzoic acid in *foods*, E. Mohler (*Bull. Soc. Chim.*, 1890, [iii], 3, 414) employs the reaction of hydrogen sulphide on an ammoniacal solution of symmetrical dinitro-benzoic acid (1 : 3 : 5), whereby reduction takes place successively to amino-nitrobenzoic and diaminobenzoic acid. In the case of beer, for example, 100 c.c. are rendered alkaline by sodium hydroxide and evaporated to a paste, which is acidified with hydrochloric acid, mixed with sand, and extracted with ether (20 c.c.). The ether is evaporated, and the residue moistened with sulphuric acid (2 c.c.), heated to 240° till acid vapours are evolved and charring takes place, when a few decigrams of sodium nitrate are gradually added till the liquid becomes colourless. The clear liquid formed is poured into excess of aqueous ammonia and a drop of ammonium sulphide added. The least trace of benzoic acid is at once indicated by the production of a yellow coloration changing to reddish-brown.

L. Robin modifies Mohler's method as follows· 50 c.c. of the liquid (beer, wine, or cider) are mixed with a little ferric chloride solution and a little hydrochloric acid, and shaken with 40–50 c.c. of ether. The ethereal extract is washed twice with water and half of it is shaken with a solution of 0.3 grm. of sodium hydrogen carbonate in a mixture of 20 c.c. of water and 5 c.c. of alcohol. The aqueous alcoholic solution is separated, evaporated to dryness, and the residue heated with 5 c.c. of sulphuric acid and 10 drops of fuming nitric acid until sulphuric acid fumes are evolved. The acid liquid is then poured into 50 c.c. of cold water, the solution made ammoniacal and treated with a solution of ammonium hydrosulphide, drop by drop, shaking after each addition. In the presence of benzoic acid, an orange-red coloration commences to appear and develops rapidly. The addition of alkaline hydrosulphide should be arrested when the colour is first observed. It is claimed that 0.001 grm. can be detected in this way (*Ann. chim. anal.*, 1909, **14**, 53).

Robin states (*Ann. Falsif.*, 1913, **6**, 277) in reference to his modification of Mohler's method that since salicylic acid and other phenolic derivatives respond to the test, these must be removed by dissolving the benzoic acid extract in dilute sulphuric acid, adding 10% potassium permanganate solution until the red coloration becomes permanent after heating at 80°, and then extracting with ether and proceeding with the test.

von der Heide and Jakob (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 137) have described the following method to detect benzoic acid in wine. A sample of the wine is made alkaline and evaporated until all the alcohol has been driven off. The residual solution is acidified, submitted to steam distillation, and the distillate extracted with ether. The ethereal solution is evaporated and the residue tested by Robin's modification of Mohler's method. The method is stated by Polenske (*Arbeit., Kaiserl. Gesundheitsamte*, 1911, **38**, 149) to be trustworthy.

Grossfield (*Zeitsch. Nahr. Genussm.*, 1915, **30**, 271–273) states that von der Heide and Jakob's variation of Mohler's test is trustworthy but tedious, and that the reduction of the dinitrobenzoic acid with ammonium sulphide has little advantage. He modifies the method as follows. The dry alkali benzoate residue is mixed with 0.1 grm. of potassium nitrate and 1 c.c. of concentrated sulphuric acid, the mixture is heated for 20 minutes on a boiling water-bath, then cooled, diluted with 2 c.c. of water, again cooled and treated with 10 c.c. of 15% ammonia and 2 c.c. of 2% hydroxylamine hydrochloride solution. A red coloration develops more or less rapidly according to the amount of benzoic acid present: the coloration develops more quickly if the mixture is heated, and reaches its greatest intensity when the mixture is cooled. The test will distinguish benzoic from salicylic acid but not from cinnamic acid or benzene.

For the detection of benzoic acid in butter G. Halphen (*J. Pharm. Chim.*, 1908, [vi], **28**, 201) has described a variation of Mohler's method in which the reduction is effected by sodium sulphite.

Halphen's method has been modified by Robin (*loc. cit.*) in order to avoid emulsification when the butter is extracted. 25 grm. of the butter are melted and poured into a solution of 0.5 grm. of sodium hydrogen carbonate in a mixture of 50 c.c. of water and 15 c.c. of alcohol. The mixture is stirred by giving the beaker a circular movement and allowed to stand for ten minutes. The aqueous-alcoholic liquid (which should be alkaline to litmus) is then separated, treated with 7 to 8 drops of dilute sulphuric or hydrochloric acid, heated just to boiling, treated with a little tripoli, and poured on to a moistened folded filter, large enough to contain it entirely. The filtrate (filtration must be repeated if necessary until the liquid is clear) is extracted with ether and the extract tested as already described.

J. de Brevans (*J. Pharm. Chim.*, 1909, [vi], **14**, 438), for the detection of benzoic acid or benzoates in foodstuffs, relies on the production of aniline blue when the acid is heated with aniline containing rosaniline hydrochloride. This author uses a mixture of equal parts of ether and petroleum spirit for the extraction. According to Halphen, the method is unsuitable for use in testing butter.

Mlle. Anna Jonescu has (*J. Pharm. Chim.*, 1909, [vi], **29**, 523) described a method of detecting benzoic acid by treating 1 c.c. of a solution (containing 1 grm. per litre) with 1 drop of officinal ferric chloride solution (1.28%) and 1 drop of a 0.3% hydrogen peroxide solution. The liquid, at first yellow, gradually (immediately on warming) assumes the violet colour characteristic of salicylic acid. The method, which cannot be employed in the presence of phenols, salicylic acid, or saccharin, is stated to be especially applicable to milk.

The test devised by Mlle. Anna Jonescu seems to meet with considerable commendation, being applied or recommended by Halphen, Marchadier, Thomann, Denigès, Biernath, Philippe and Fleury. On the other hand, Fischer and Gruenert state that it is far inferior to the modified Mohler method.

Fleury (*J. Pharm. Chim.*, 1913 [vii], **8**, 460) points out that the Jonescu reaction takes place very slowly in cold solutions, whilst heat is liable to carry it too far and so to cause failure. He hastens the action by the addition of a trace of ferrous sulphate to act as catalyst. 10 c.c. of the solution to be tested (containing 1–5 mg. of benzoic acid) are treated with 3 drops of a solution of ferric chloride (sp. gr. 1.260, containing about 26% of the anhydrous salt) diluted 1 to 10, then with 3 drops of a solution of hydrogen peroxide (12 vol.) also diluted 1 to 10, and finally with 3 drops of 3% solution of ferrous sulphate. The reagents should be added in the order named, shaking after each addition. In about 30 seconds action commences, and the violet coloration attains its maximum in 5– 0 minutes. The test is sensitive to 0.0002 grm. of benzoic acid.

Denigès (*Bull. Soc. Pharm. de Bord.*, 1911, 249; *Pharm. J.*, 1911, **87**, 201) publishes the following modification of Jonescu's method. To 4 c.c. of an aqueous solution supposed to contain benzoic acid, 0.2 c.c. of 20% (by volume) acetic acid, 0.2 c.c. of ferric chloride solution (dilute) and 0.2 c.c. of hydrogen peroxide solution (one volume) are added and the mixture is boiled for 10–15 seconds. A violet coloration is obtained even when the solution contains not more than 0.0005 grm. of benzoic acid per 1 c.c. In cases where smaller quantities are to be detected a blank experiment should be made simultaneously, both test-tubes being heated in boiling water for the same length of time.

Halphen (*Matières grasses.*, 1910, **3**, 1761) points out that if in preparing the solution for the Jonescu test ammonia is used to neutalise the acid before evaporating to dryness, 0.001 grm. of benzoic acid will fail to give the test, whilst by using sodium hydroxide a sharp indication is obtained.

Baumann and Grossfield have investigated (*Zeitsch. Nahr. Genussm.*, 1915, **29**, 397–409) several methods which have been described for the detection of benzoic acid in foods, particularly those described by Mohler, Jonescu, and von der Heide and Jakob. They give preference to Mohler's method, a reaction being obtained with 0.1 mg. of benzoic acid. In certain cases Jonescu's test fails to detect the presence of relatively large quantities (some mg.) of the acid.

For the detection of benzoic acid in milk Revis (*Analyst*, 1912, **37**, 346) has devised the following process. At least 100 c.c. of the milk are diluted with an equal volume of water, 5 c.c. of a 10% solution of sodium carbonate are added, and the mixture is heated in boiling water for 2–3 minutes. 10 c.c. of a 20% solution of calcium chloride are added, the heating is continued until the casein is completely coagulated, the liquid cooled and filtered, and the filtrate made neutral to litmus paper with hydrochloric acid. To the neutral filtrate 10 c.c. of copper sulphate solution (as made for Fehling's solution) and 10 c.c. of potassium hydroxide solution (containing 31.18 grm. per litre) are successively added and the liquid again filtered. The filtrate is transferred to a separating funnel, acidified with hydrochloric acid and shaken with 50 c.c. of ether. The aqueous solution is run off, the ether washed three times with a little water, 10 c.c. of water and a drop of phenolphthaleïn solution are added, and a saturated solution of barium hydroxide is run in gradually, with shaking, until a permanent pink colour is produced. The aqueous layer is now filtered into a porcelain basin, evaporated to about 5 c.c., filtered into a test-tube and 1% acetic acid added until the liquid is decolourised. Two more drops of the acetic acid are then added, and 1 drop of a freshly prepared neutral solution of ferric chloride (10%). With as little as 0.02% of benzoic acid the characteristic precipitate of ferric benzoate is obtained. In examining cream 50 c.c. are diluted with water to 20 c.c. and then treated as above.

Philippe (*Mitt. Lebensmittel-unters. Hyg.*, 1911, **2**, 377. *J. Pharm. Chim.*, 1915, [vii], 168–169) extracts the benzoic acid from the milk by a similar method and identifies it by Robin's or Jonescu's test, or by sublimation.

According to Hinks (*Analyst*, 1913, **38**, 555) 0.01% or more benzoic acid in milk or cream can be detected as follows: 25 c.c. of the milk or from 10 to 20 grm. of the cream are heated with an equal volume of concentrated hydrochloric acid until the curd has completely dissolved. The liquid is cooled, shaken with 25 c.c. of a mixture of petroleum spirit (2 vols.) and ether (1 vol.), the ethereal solution separated and shaken with 1 drop of ammonia and 5 c.c. of water. The aqueous layer is now separated, heated on a water-bath for a few minutes to expel the excess of ammonia and then tested with ferric chloride solution. On adding the ammonia, ammonium benzoate is precipitated and this test although less characteristic is more sensitive than the ferric chloride test.

For the detection of benzoic acid in butter, methods are described by Marchadier (*Ann. Falsif.*, 1911, **4**, 28) and Biernath (*Apoth. Zeit.*, 1912, **27**, 192) in which the sample is distilled with water, a little sulphuric acid and a small quantity of pumice-stone and the distillate tested by Jonescu's method. Biernath states that the reaction is retarded by mineral acids, volatile organic acids and alcohol.

Friese (*Pharm. Zentr.*, 1911, **52**, 1201) and Volhase (*Chem. Zeit.*, 1913, **37**, 312) have described other methods of detecting benzoic acid in fats, but these are similar to that of Fischer and Gruenert.

According to Stadlin (*Chem. Zeit.*, 1916, **40**, 770) small quantities of benzoic acid are more conveniently isolated from fats by dialysis than by extraction. 20–30 grms. of the semi-melted fat are spread in an even layer over the parchment diaphragm of a Kreis dialyser and covered with 50% alcohol. The outer chamber of the dialyser is charged with alcohol of the same strength and after 24 hours the dialysate is rendered slightly alkaline and evaporated to expel the alcohol, the volume of the liquid being maintained by the addition of water. It is then made slightly acid, shaken twice with ether and the extracts evaporated at a low temperature. The residue, which crystallises in groups of fine needles, is then tested for benzoic acid by oxidation to salicylic acid by the Jonescu and Fleury method. It is dissolved in 10 c.c. of water and treated with 3 drops of dilute (1:10) hydrogen peroxide solution, 3 drops of dilute (1:10) official ferric chloride solution and 3 drops of 3% ferrous sulphate solution. The violet coloration due to salicylic acid appears after about 0.5 minute. If salicylic acid is also suspected, the same method is used with the exception that the ferric chloride solution is applied prior to the oxidation with hydrogen peroxide.

K. Fischer and O. Gruenert (*Zeitsch. Nahr. Genussm.*, 1909, **17**, 721) advocate the following method for the extraction of benzoic acid from flesh products: 50 grm. of the finely divided material are mixed with 100 c.c. of 50% alcohol, the mixture acidified with dilute sulphuric acid and stirred for 30 minutes. It is then filtered through muslin, the solid pressed, the expressed liquid made alkaline, and all the alcohol expelled by evaporation on a water-bath. When the volume has been reduced to 50 c.c., 5 grm. of sodium chloride are added, the liquid acidified with dilute sulphuric acid and heated to boiling. After cooling, the liquid is filtered, the filtrate extracted with ether, the ethereal extract washed with water and evaporated at a low temperature. For the identification of the acid in the residue, these authors prefer to convert it into salicylic acid by fusion with sodium hydroxide, the latter being recognised by the ferric chloride reaction. It is stated that de Brevans' test is useless for the detection of benzoic acid in meats and fats.

Fischer and Gruenert (*Zeitsch. Nahr. Genussm.*, 1912, **20**, 580) find that the methods of Halphen and Robin which are applicable to butter are entirely inapplicable to meats and other fats. On the other hand, von der Heide and Jakob's modification of Mohler's method gave a sharp indication with as little as 0.01% of benzoic acid in 50 grm. of substance. The authors prefer to extract the preservative from meats by the method previously described, but for butter and margarine they recommend the following process: 50 grm. of butter are introduced into a 300 c.c. Erlenmeyer flask, treated with 150 c.c. of 1% sodium hydrogen carbonate solution and boiled for 5 minutes with frequent shaking. If necessary a blast of air is used from time to time to prevent frothing. The hot liquid is transferred to a separating funnel and the aqueous layer drawn off, neutralized with N/2 sulphuric acid solution, using methyl-orange as indicator, and clarified by adding 10 c.c. of Fehling's copper sulphate solution and 10 c.c. of potassium hydroxide solution (containing 31.15 grm. per litre). The liquid, which should be neutral or faintly acid, is filtered, the filtrate acidified with dilute sulphuric acid and extracted with ether. The ethereal extract is washed, evaporated and the residue tested by von der Heide and Jakob's method.

F. Marre has described (*Ann. Falsif.*, 1915, **8**, 15–27) the following method of detecting benzoic acid in preserved meats. An average sample of 20 grm. is dried completely, mixed with sand, and extracted with benzene or carbon tetrachloride to remove fat, four extractions being made, each with 20–30 c.c., the first for 30 minutes the others for five minutes each. The material is then heated to evaporate the solvent, moistened thoroughly with 10% sulphuric acid and extracted with hot water. The aqueous extract is shaken with ether, the ethereal solution evaporated and the residue dissolved in a small quantity of aniline faintly coloured with magenta, adding water and hydrochloric acid sufficient to dissolve the aniline. The mixture is filtered and the filter washed with water; if benzoic was present in the sample, the filter paper is coloured blue owing to the formation of aniline blue. Benzoic acid may be detected in the presence of nitrates by extracting the meat with water, evaporating the aqueous extract to a small volume, transferring this to a test-tube and evaporating to dryness; when the residue is incinerated, an odour of bitter almonds indicates the presence of a derivative of benzoic acid or of an amino-benzoic acid.

Lythgoe and Marsh (*J. Ind. Eng. Chem.*, 1911, **3**, 842) have observed that when the ethereal extract of coffee or pure coffee extract is treated with ferric chloride solution in the usual manner for the detection of benzoic acid, a precipitate is obtained which differs from ferric benzoate in colour, and yields crystals different from those of benzoic acid on sublimation. The ammonium salt of the substance which produces this precipitate is distinguished from ammonium benzoate in that it gives precipitates with manganese, nickel, magnesium, calcium, barium and strontium. Accordingly when looking for benzoic acid in coffee extract these authors recommend that the acid solution should be extracted several times with ether, the ether extract washed with water and extracted with ammonia. The ammoniacal solution is evaporated to a small volume, adding ammonia to prevent development of acidity, and treated with a solution of manganese sulphate. It is then filtered and the filtrate tested for benzoic acid with ferric chloride solution.

A new test for benzoic acid has been discovered by Schmatolla (*Pharm. Zeit.*, 1913, **57**, 947). If 20 c.c. of a solution containing benzoic acid are treated with 5 c.c. of hydrogen peroxide solution, and then with freshly prepared solution of 5 grm. of ferrous sulphate and 5 grm. of boric acid in 100 c.c. of water, a blue or greenish-blue colour appears in a few seconds.

A new method of detecting benzoic acid, especially adapted to the toxicological recognition of cocaine and stovaine (which contain a benzoyl group) or atropine (which yields benzoic acid on oxidation) has been described by Guerbet (*Compt. rend.*, 1920, **171**, 40–41). The small amount of material is placed on a watch-glass, 3 or 4 drops of nitric acid (sp. gr. 1.49) are added, and the mixture evaporated to dryness on a water-bath. The residue is taken up with one drop of a 10% solution of stannous chloride, and after two or three minutes warming the nitrobenzoic acids are reduced. The liquid is allowed to cool and two drops of a 1% solution of sodium nitrite are added and finally three drops of a 1% solution of β-naphthol in 10% ammonia, when a bright orange red precipitate is obtained if benzoic acid or one of the alkaloids mentioned above was originally present. The test may be confirmed by dissolving the azo-compound in 1 c.c. of concentrated sulphuric acid and pouring the solution into water, an orange yellow colour resulting. For toxicological work the test may be applied to the extracts of organs prepared by Stas' method.

Estimation. Volumetric Methods.—Benzoic acid is distinctly acid to methyl-orange, but this indicator cannot be employed for its titration, as the end point is very indefinite. Benzoic acid is sharply mono-basic towards phenolphthalein and Poirrier's blue, and may be accurately titrated by sodium hydroxide with the aid of either of these indicators.

The benzoic acid, liberated if necessary by acidification, is dissolved by repeated agitation with ether, chloroform, or benzene. After washing the ethereal solution with water, the benzoic acid may be estimated by adding alcohol and titrating with standard sodium hydroxide and phenolphthalein.

An iodometric method of estimating benzoic acid has been described by Remy (*Apoth. Zeit.*, 1911, **26**, 835). The acid (0.05–0.5 grm.) is dissolved in 30 c.c. of 50% alcohol. 5–10 c.c. of 5% potassium iodide solution and an equal volume of 5% potassium iodate solution are added and the liberated iodine titrated with thiosulphate solution. The benzoic acid is converted into monoiodobenzoic acid, and one molecule of benzoic acid is equivalent to one atom of iodine.

For the estimation of benzoic acid in benzoates Lyons (*J. Amer. Pharm. Assoc.*, 1912, **1**, 526) dissolves 0.25 grm. of the salt in 10 c.c. of water in a separating funnel, acidifies with 25 c.c. of N/10 sulphuric acid solution and extracts four times with chloroform (which must be neutral). The chloroform is run into a second separating funnel, washed with 20 c.c. of water, transferred to a flask and titrated with N/25 alkali solution using methyl-red as indicator. The end point of the titration is indicated by the appearance of a yellow colour in the aqueous layer after shaking with the chloroform.

E. B. R. Prideaux and A. O. Bentley have described (*Pharm. J.*, 1923, **110**, 427–430) two volumetric methods for the estimation of both alkali and acid in organic alkali salts such as salicylates or benzoates. In the first method the organic acid is precipitated with a known excess of standard hydrochloric acid and collected on a filter and washed free from mineral acid. The filtrate and washings are extracted with chloroform, the aqueous portion is titrated with standard alkali to give the total alkali, and the chloroform extract and the precipitated acid are titrated with standard alkali to give total acid. In the second method both alkali and organic acid are titrated in the same sample in the presence of chloroform and suitable indicators. Thus with sodium benzoate, for example, good results are obtained by titrating first with N/1 hydrochloric acid, with bromophenol blue as indicator, to the production of a blue colour, then adding phenolphthalein and titrating the liberated organic acid with N/1 sodium hydroxide solution to the first formation of a pink colour.

As the result of a critical examination of the methods of estimating benzoic acid in foods W. von Genersich (*Zeitsch. Nahr. Genussm.*, 1908, **16**, 224) concludes that it is most completely extracted with benzene. To facilitate the penetration of the solvent, it is advantageous to subject fatty substances to a preliminary boiling with sodium hydroxide solution. One or two drops of phenolphthalein solution are added to an aliquot part of the benzene extract and the liquid titrated with N/10 potassium hydroxide solution. (1 c.c. corresponds to 0.0122 grm. of benzoic acid.)

K. Baumann and J. Grossfield recommend (*Zeitsch. Nahr. Genussm.*, 1915, **29**, 397–409) the following method for the estimation of benzoic acid in animal foods.

Milk.—100 c.c. of the milk are treated with phenolphthalein solution and concentrated potassium carbonate solution is added until a permanent red coloration is obtained; the mixture is then diluted to

200 c.c., 20 c.c. of 20% calcium chloride solution added, and the mixture heated on a water-bath for 15 minutes, cooled and diluted to 250 c.c. The mixture is now filtered (old milks sometimes yield a turbid filtrate but this does not affect the process) 175 c.c. of the filtrate are transferred to a 200 c.c. flask, a few drops of copper sulphate solution (to remove hydrogen sulphide) and 10 c.c. of sodium phosphotungstate solution (200 grm. of sodium tungstate and 120 grm. of sodium phosphate per litre) are added and the contents of the flask are diluted with sulphuric acid (1:3) to 200 c.c. After 18 hours the mixture is filtered, 100 c.c. of the filtrate are percolated with carbon tetrachloride for 6 hours the latter is separated, mixed with an equal volume of neutral alcohol containing phenolphthalein, and the solution is titrated with N/10 alkali hydroxide solution. Milk free from benzoic acid yields a carbon tetrachloride extract which requires 0.1 c.c. of N/10 alkali solution for neutralisation; allowing for this correction the quantity of benzoic acid present in a sample is found from the equation $x = 0.03486(n - 0.1)$ grm. where n = c.c. of N/10 alkali solution used.

Fats, etc.—50 grm. of the fat such as butter or margarine are melted in a beaker, dissolved in 150 c.c. of benzene, the solution washed with ether into a separating funnel (any insoluble portion may be left in the beaker) and shaken with 20 c.c. of warm potassium carbonate solution containing phenolphthalein; if the red coloration disappears, more potassium carbonate solution must be added. The aqueous layer is then drawn off into the beaker, and the fatty layer is extracted several times with hot water. The united aqueous extracts are then treated with 20 c.c. of 20% calcium chloride solution, a few pieces of pumice stone are added and the solution is evaporated in a basin until all odour of benzene has disappeared. The solution is now transferred to a 200 c.c. flask and the process continued as described under milk. The quantity of benzoic acid present is calculated from the equation $x = 0.02788(n - p)$ grm.; where p is the number of c.c. of N/10 alkali used by 100 grm. of different fats free from benzoic acid. For lard the correction is 0.05 c.c., for butter 0.50 c.c., and for palm oil 0.30 c.c.

O. Kopke and E. Bodlander have described (*Zeitsch. Nahr. Genussm.*, 1922, **43**, 345–350) the following method of estimating benzoic acid in margarine. 50 grm. of the latter and 100 c.c. of N/10 sodium bicarbonate solution are heated at 60° on a water-bath in a stoppered 300 c.c. flask and shaken strongly for about 2 minutes. After cooling and filtering through a dry filter, 75 c.c. of the aqueous layer are poured into a 100 c.c. measuring flask containing about 30 grm. of pure ammonium sulphate, strongly shaken and allowed to stand about 30 minutes. When the ammonium sulphate has dissolved the solution is diluted to the mark and again filtered through a dry filter. 80 c.c. of the filtrate are acidified with 3 c.c. of dilute sulphuric acid and extracted five times with 40 c.c. of a mixture of equal volumes of ether and of petroleum spirit boiling below 60°. The ethereal extract is washed three times with 5 c.c. of water to remove traces of sulphuric acid and the solvent evaporated off slowly on a water-bath, the last fraction being removed at room temperature in a current of air. The residue is dissolved in water and titrated boiling with N/10 sodium hydroxide solution, using phenolphthalein as indicator; preferably, a slight excess of the alkali solution is first added to prevent loss of benzoic acid and the solution titrated first with N/10 acid until the red colour disappears and then with N/10 alkali. The object of the addition of ammonium sulphate is to remove albuminous and other matter, which would otherwise lead to the formation of emulsions. The percentage of benzoic acid is given by $a \times 0.012208 \times (100 + w/2)/30$ where a is the number of c.c. of N/10 sodium hydroxide solution used and w the percentage of water in the margarine.

Whilst extraction with chloroform can be applied to the estimation of benzoic acid in cranberries, Folin and Flanders (*J. Amer. Chem. Soc.*, 1911, **33**, 1622) found that certain precautions have to be taken in the case of ketchups, from which chloroform extracts other acids also. 25 grm. of the ketchup are placed in a 50 c.c. beaker, treated with 2 c.c. of concentrated nitric acid and about 0.2–0.3 grm. of sodium nitrite added in small portions, the mixture being well stirred after each addition. The liquid is rinsed into a 500 c.c. separating funnel with the help of 200 c.c. of saturated ammonium sulphate solution, and is then extracted five times with chloroform (50 c.c., 35 c.c., 25 c.c., 25 c.c., 25 c.c.). The chloroform is run into another separating funnel and shaken with 200 c.c. of a saturated solution of sodium chloride made faintly acid with hydrochloric acid. It is then transferred to a third separating funnel, again shaken with 200 c.c. of the acidified salt solution, and finally run into a 500 c.c. Erlenmeyer flask and titrated with standard alcoholic sodium ethoxide solution in the presence of phenolphthalein.

Cinnamic acid is not removed by the washing with salt solution; hence any present will be estimated with the benzoic acid. The sodium ethoxide solution is prepared by dissolving 2–3 grm. of sodium in a litre of absolute alcohol; it is standardised against benzoic acid in chloroform solution.

Raiziss and Dubin (*J. Biol. Chem.*, 1915, **20**, 125) sought for a solvent which would not form emulsions with urine. They found that toluene is preferable to the chloroform recommended by Folin and Flanders. 100 c.c. of fresh urine are acidified with 1 c.c. of concentrated nitric acid, then saturated with ammonium sulphate (50–60 grm. being required) and extracted four times with toluene (50 c.c., 40 c.c., 30 c.c., and 30 c.c.). The toluene extracts are mixed and washed with 100 c.c. of saturated salt solution containing 0.05% of concentrated hydrochloric acid. The washing is repeated and then the benzoic acid in the toluene solution is titrated with N/20 sodium ethoxide solution using phenolphthalein as indicator. The ethoxide solution is prepared by dissolving 2.3 grm. of sodium in alcohol and diluting the solution to 2000 c.c. Hippuric acid is not extracted by toluene under the above conditions.

A method of estimating benzoic acid in blood and tissue has been described by F. B. Kingsbury (*J. Biol. Chem.*, 1915, **21**, 289–295).

McAbee (*J. Ind. Eng. Chem.*, 1910, **2**, 544) has applied the provisional A. O. A. C. method of estimating sodium benzoate to ketchups containing added known weights of the salt and has shown that the method is reliable.

To estimate salicylic and benzoic acids and saccharin in fruit juices, jams, and lemonades, van Raalte recommends (*Chem. Weekblad.*,1912, **9**, 1004) boiling these substances for 5 hours with dichloroethylene followed by titration with N/10 alkali solution and phenolphthaleïn. Then the neutral aqueous liquid, after separation from the dichloroethylene, is examined for the two acids and saccharin. The latter can be extracted with ether after addition of phosphoric acid.

In a report (*U. S. Dept. Agr. Bur. Chem., Bull.* 137, 108) on cooperative work on the determination of sodium benzoate in jams, jellies, and salt codfish, Dunbar advocates making the former two substances alkaline with milk of lime instead of sodium hydroxide, the latter being used with codfish. The sodium benzoate is then extracted with a definite volume of water, of which an aliquot part is saturated with sodium chloride, filtered, acidified and extracted with chloroform, the chloroform solution being evaporated and the residue titrated.

Van der Laan and Tijdens (*Chem. Weekblad.*, 1910, **7**, 603) recommend extracting benzoic acid from foods by means of benzene for quantitative estimation.

Polenske (*Arbeit. Kaiserl. Gesundheitsamte*, 1911, **38**, 149) has described a method of estimating benzoic acid in cranberries.

It has been shown by E. Schowalter (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 185–194) that, whilst the presence of saccharin interferes with the estimation of benzoic acid by the methods described by Mohler, Grossfield and von der Heide, the two substances may be separated from one another by taking advantage of the insolubility of saccharin in carbon tetrachloride. The residue obtained on evaporating the ethereal solution of the two substances at a low temperature is dried under reduced pressure to remove the last traces of ether and acetic acid, and is then treated with carbon tetrachloride; the benzoic acid dissolved by this solvent may be estimated by titration. Saccharin cannot be separated from benzoic acid by sublimation, since both begin to sublime at about 120°.

Gravimetric Methods.—Benzoic acid may be *separated* from fixed substances by sublimation, and may be estimated in gum benzoin by that means.

Benzoic acid may also be approximately estimated, in the absence of interfering substances, by converting it into a soluble neutral benzoate, and precipitating the cold solution with lead acetate, avoiding excess. The precipitate is filtered off, washed once with cold water, then with proof-spirit containing 0.5% of acetic acid, and finally dried at 100° and weighed. Its weight, multiplied by 0.5432 gives the amount of benzoic acid present.

Neutral benzoates are precipitated tolerably perfectly by cupric acetate or sulphate, especially in presence of alcohol, and the reaction may be employed for the estimation of benzoic acid.

After extracting the benzoic acid from its acidified solution with ether, sodium hydroxide or baryta may be added to the ethereal layer with constant agitation until the liquid is exactly neutral (to phenolphthalein). The ethereal layer (which will retain any benzaldehyde or essential oils) is separated and the aqueous liquid evaporated to dryness, the residue dried at 100°, and the benzoate weighed.

F. M. Horn (*Zeit. Chem. Ind.*, 1888, **2**, 329) recommends the following method of estimating benzoic acid in milk: About 10 c.c. diluted with an equal volume of water are warmed with dilute hydrochloric acid (1%) until it coagulates. After filtering and washing the precipitate with warm water, the filtrate is evaporated and the residue taken up in 50% alcohol. A few drops of ammonia are added to this solution after filtration, the excess boiled off, and the liquid exactly neutralised and treated with its own volume of absolute alcohol. The benzoic acid is precipitated with copper sulphate and weighed on a tared filter as copper benzoate.

Hinks (*Analyst*, 1913, **38**, 555) states that the benzoic acid present in milk may be estimated by heating 25 c.c. with hydrochloric acid in a reflux apparatus, extracting the cooled solution three times with 20 c.c. of a mixture of ether (1 vol.) and petroleum spirit (2 vols.) and shaking the separated ethereal solutions with 10 c.c. of water and 1 drop of ammonia; this extraction is twice repeated. The mixed aqueous portions are then acidified with hydrochloric acid, extracted three times with the ethereal solvent, the extracts evaporated at ordinary temperature and the residue dried in a desiccator to constant weight. The benzoic acid is then volatilised at 100° and its amount determined by the loss in weight.

Liverseege and Evers (*J. Soc. Chem. Ind.*, 1913, **32**, 319) have described an empirical method of estimating benzoic acid in milk, by which, however, only about 45% of the acid is obtained.

For the estimation of benzoic acid in ketchup La Wall and Bradshaw (*Amer. J. Pharm.*, 1908, **80**, 171) recommend the following method: 20 grm. of the sample are mixed with 5 c.c. of hydrochloric acid and 25 c.c. of a saturated solution of sodium chloride, the mixture shaken for 5 minutes and poured on to a moistened filter. The residue on the filter is washed with saturated salt solution until the filtrate and washings amount to 100 c.c. The latter is shaken 3 times with chloroform, and the united extracts evaporated at ordinary temperature. The residue is dried to constant weight over sulphuric acid. It is usually white and crystalline, but if yellow and oily, it should be dissolved in ammonia, the solution acidified with sulphuric acid and the extraction with chloroform repeated. The estimation may be confirmed volumetrically by dissolving the weighed residue in a little alcohol and titrating with N/20 potassium hydroxide solution, using phenolphthalein as indicator. After titration it is advisable to divide the neutral solution into 2 parts, 1 of which is tested for cinnamic acid by adding manganous sulphate solution, and the other for salicylic acid by adding excess of ferric chloride solution. Saccharin and salicylic acid if present in the ketchup are extracted with the benzoic acid and must be estimated separately, and the quantities found deducted from the total weight of the residue.

Another method of estimating benzoic acid in ketchup is described by Reed (*J. Amer. Chem. Soc.*, 1907, **29**, 1626), but this is a lengthy process and requires a flask of a special pattern.

Hillyer (*J. Ind. Eng. Chem.*, 1909, **1**, 538), has devised a method of estimating benzoic acid in ketchups depending on the precipitation of the acid from alcoholic solution as silver benzoate and weighing as such. To estimate benzoic acid in chopped meat Krüger (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 12) recommends the following out of several modifications of the distillation method. 50 grm. of the chopped meat are mixed with enough sulphuric acid, making allowance for the moisture content of the sample, to have present 45 c.c. of 70% sulphuric acid. The mixture is heated until clear and then steam distilled (keeping the volume constant) until 500 c.c. of distillate have been collected. The cold distillate is filtered and the filter washed, the filtrate made faintly alkaline with sodium hydroxide solution and evaporated to small bulk on a water-bath. To remove impurities, a cold saturated solution of potassium permanganate is added until the red colour produced persists for 5 minutes. The excess of permanganate is destroyed with sodium sulphite solution and the liquid evaporated to 10 c.c. After cooling it is transferred to a separating funnel and acidified with dilute sulphuric acid (1:3). The manganese precipitate, remaining in the basin is dissolved in cold saturated sodium sulphite solution and sulphuric acid and transferred to the funnel. The liquid is extracted three times with an equal volume of a mixture of ether and petroleum spirit, the ethereal solution washed three times with 3 c.c. of water and dried with a small amount of powdered gum tragacanth. It is then allowed to evaporate spontaneously in a tared basin, dried and weighed. The results can be checked by subliming the product and reweighing or by titration. From 97 to 120% of the benzoic acid present is recovered by this method.

METALLIC BENZOATES

The metallic benzoates are mostly crystallisable and soluble in water and alcohol, but insoluble in ether. Some of them, such as the sodium and barium salts, are withdrawn from their solutions by animal charcoal, and calcium benzoate is decomposed by it, so that free benzoic acid can be extracted by treating the charcoal with ether.

The general reactions and methods of analysing metallic benzoates have already been described above.

Commercial benzoates are liable to contain much the same impurities as benzoic acid (page 372), especially *hippuric* and *chlorobenzoic acids*, *sulphates*. and *chlorides*. The two former impurities may be detected by acidifying the solution of the benzoate with hydrochloric acid and agitating with ether. Benzoic and chlorobenzoic acids pass into the ethereal layer, whilst hippuric acid remains (undissolved) in the aqueous liquid. The chlorobenzoic acid or other organic chlorine compounds may then be detected by allowing the bulk of the ether to evaporate spontaneously, adding alcohol, igniting, and testing the products of combustion for hydrochloric acid, as described above.

Sodium benzoate, $NaC_7H_5O_2 + H_2O$, crystallises in colourless needles. The salt is soluble in 1.7 parts of water at 15° if the acid used for its preparation were pure, but has a lower and varying solubility if chlorobenzoate or hippurate be present. Sodium benzoate receives an extensive application in America in the preservation of articles of food (see page 371).

The British Pharmacopœia 1914 fixes the following standard of purity for the sodium and ammonium salts:

Sodium Benzoate.—"Loses not more than 4% of its weight when dried at 112°. 1 grm. of this dried salt heated to redness until gases cease to be evolved leaves an alkaline residue which treated with water, filtered and well washed, yields a clear solution requiring for neutralisation not less than 13.7 c.c. nor more than 13.9 c.c. of N/2 solution of sulphuric acid. Yields no characteristic reactions for copper, iron, potassium or carbonates, and not more than the slightest reactions for chlorides or sulphates. Lead limit 10 parts per million. Arsenic limit 2 parts per million."

Ammonium Benzoate.—"If 1 grm. is dissolved in 20 c.c. of water and excess of nitric acid added a crystalline precipitate of benzoic acid separates, the filtrate from which remains clear on the addition of solution of barium chloride, and does not become more than slightly opalescent on the addition of solution of silver nitrate. Lead limit 10 parts per million. Arsenic limit 2 parts per million."

Potassium benzoate, $KC_7H_5O_2 + 3H_2O$, forms concentrically grouped needles.

Lithium benzoate forms a crystalline powder or small shining scales, soluble in 4 parts of cold or 25 of boiling water and in 12 parts of cold or 10 of boiling alcohol. It is liable to contain the same impurities as sodium benzoate (see above) and lithium citrate (Vol. 1).

Calcium benzoate, $Ca(C_7H_5O_2)_2 + 3H_2O$, crystallises in granules or feathery needles, and is less soluble in hot water than in cold.

Manganous benzoate is soluble in water (distinction from cinnamate).

Ferric benzoate is obtained as a flesh-red precipitate by mixing solutions of neutral benzoates and ferric chloride. It is decomposed by washing with water into a soluble acid and an insoluble basic salt.

Cupric benzoate, $Cu(C_7H_5O_2)_2 + 2H_2O$, crystallises from hot water in light blue needles or plates united in spherical masses. It is one of the least soluble of the benzoates.

Lead benzoate is crystalline and difficultly soluble.

Mercuric benzoate, $Hg(C_7H_5O_2)_2$, forms long silky crystals soluble in hot water, but very sparingly soluble in cold water. It is more readily dissolved by water containing chlorides or iodides. According to Rebière (*Pharm. Jour.*, 1887, **1**, 82), mercuric benzoate, as met with in commerce, is of very variable composition, as exemplified by the following analyses:

	A	B	C	D	Theory
Mercury	54.78	52.80	42 60	45.12	45.25
$C_7H_5O_2$	24.80	23.20	58.00	54.75	54.75
HCl	16.79	traces	traces	....	....
HNO_3	traces	20.36	traces	....	....

The salt can be obtained of almost theoretical composition (as was sample D) by precipitating mercuric chloride with excess of sodium hydroxide, washing the mercuric oxide till free from chlorine, and boiling it with the calculated quantity of powdered benzoic acid in a little water, leaving the oxide in slight excess. On boiling the resulting powder with a large quantity of water it dissolves, and, on cooling, pure mercuric benzoate crystallises out.

Bismuth Benzoate.—A basic salt, stated to have the composition $BiO.C_7H_5O_2$, is officinal in France. It is prepared by treating benzoic acid with freshly prepared moist bismuth hydroxide. The salt is amorphous, and commercial samples show somewhat varying composition.

BENZOIC ESTERS

Benzoic esters are obtained by the general methods used to prepare this class of compounds.

Methyl benzoate, $C_6H_5.CO_2Me$, an aromatic liquid boiling at 199°, is used to a limited extent in the preparation of artificial fruit essences and flavourings.

Ethyl benzoate, $C_6H_5.CO_2Et$, is a very fragrant liquid, boiling at 213°. It is employed in the production of artificial fruit essences (see Vol. 1), but is valueless in perfumery.

Propyl benzoate boils at 229°, and *butyl benzoate* at 247°.

Benzyl benzoate, $C_6H_5.CO_2C_7H_7$, is a natural constituent of Peru and Tolu balsams. It forms compact lustrous crystals of aromatic odour, melts at 20° to 21°, and boils at 323°. At its m. p. it has a sp. gr. of 1.227.

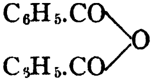
The so-called "cinnamein" of Peru balsam consists of a mixture of benzyl benzoate and cinnamate, in which the former constituent largely predominates. Benzyl benzoate is the constituent to which the efficacy of Peru balsam in the treatment of scabies is due. The synthetic ester has the advantage of being of constant composition and free from colour and odour, whilst it does not cause the irritation, due to the presence of free acid, which is sometimes a consequence of using Peru balsam. Benzyl benzoate has been introduced into commerce by the Berlin Aniline Company under the name of "*Peruscabin.*" A 25% solution of the ester in castor oil is known as "*Peruol.*"

Eugenyl benzoate, $C_{10}H_{11}O.C_7H_5O_2$, prepared by heating together eugenol and benzoyl chloride, forms the "*Benzeugenol*" of medicine. It has been employed as an antiseptic in cases of tuberculosis. It forms colourless, odourless, bitter crystals, very slightly soluble in water, but easily soluble in hot alcohol, ether, chloroform, and acetone. Benzeugenol melts at 70.5°, and gives a purple colouration with strong sulphuric acid. The formation of eugenyl benzoate is the basis of Thoms' method for the estimation of eugenol in essential oils.

Guaiacyl benzoate, or benzoyl-guaiacol, $C_6H_4(OCH_3).O.CO(C_6H_5)$, also called "*Benzosol,*" is recommended as a useful substitute for guaiacol in phthisis. It has the advantage over the latter of being tasteless and odourless. Benzosol forms small colourless crystals, melting at 57°. It is almost insoluble in water, but is readily soluble in hot alcohol, ether, and chloroform.

According to Dragendorff (*Arch. Pharm.*, 1895, **233**, 612) benzoyl-guaiacol gives a reddish-purple colour when moistened with sulphuric acid and acetone; a violet colour striped with green and violet-blue, with ferric chloride; an orange and green colour with nitric acid; a green, violet, and yellow colour with potassium nitrite; a bright red colour with sucrose or dextrose; a violet to red colour with Fröhde's reagent; and a violet, green, and blue colour with sulphovanadic acid.

Benzoic Anhydride. Benzoyl Oxide.



$$\left.\begin{matrix} C_6H_5.CO \\ C_6H_5.CO \end{matrix}\right\rangle O$$

This substance is prepared according to methods described by Gerhardt (*Annalen*, 1853, **87**, 73), Lachowicz (*Ber.*, 1884, **17**, 1282) and Minunni (*Gazzetta*, 1890, **20**, 655; 1892, **22**, ii, 213).

Benzoic anhydride crystallises in rhombic prisms melting at 42°. It boils at 360°, and dissolves readily in alcohol or ether. It is but little affected by cold water, but on boiling with water readily undergoes hydrolysis with formation of benzoic acid. By boiling with alcohol it yields *ethyl benzoate.* This and similar reactions render benzoic anhydride a valuable reagent for the production of benzoic esters, and it is employed for that purpose in the investigation of essential oils.

Benzoyl Chloride. Benzoic Chloride. $C_6H_5.COCl$.

Benzoyl chloride may be prepared by the action of phosphoric chloride on benzoic acid (Cahours, *Annalen*, 1849, **70**, 40), or by the action of chlorine on benzaldehyde. It is a liquid of penetrating odour. It boils at 198°, and solidifies at a low temperature, the solid melting at −1°. It is isomeric with the *chlorobenzaldehydes,* $C_6H_4Cl.CHO$, and is a valuable reagent in organic synthesis.

Commercial benzoyl chloride is usually contaminated with chlorobenzoic chloride, and frequently with benzaldehyde and its chloro-derivatives. These impurities cause synthetic compounds prepared with it to contain chlorine compounds difficult to remove.

Benzoic Aldehyde. Benzaldehyde

C_7H_6O; *i. e.*, $C_6H_5.CHO$

Benzaldehyde forms the major part of the essential oils of bitter almond, cherry-laurel, peach kernels, and many other vegetable products, especially of members of the natural order *Rosaceæ.*

It is manufactured synthetically chiefly by the action of lead or copper nitrate on benzoyl chloride. (Compare Lauth and Grimaux, *Bull. Soc. Chim.*, 1867, [i], **7**, 106; Piria, *Annalen*, 1856, **100**, 105; and Anschütz, *Annalen*, 1884, **226**, 18.)

Pure benzaldehyde is a thin colourless liquid of high refractive power. It has a peculiar, very agreeable odour like that of bitter-almond oil, and a burning aromatic taste. Its sp. gr. is 1.0636 at 0° and 1.0504 at 15°. It solidifies at $-13.5°$ and boils at 179°. Benzaldehyde is soluble in about 300 parts of water, and is miscible in all proportions with alcohol and ether.[1]

Synthetic benzaldehyde is largely used, for flavouring and perfumery purposes, as a cheap substitute for the natural essential oil of almonds. Most of the synthetic benzaldehyde of commerce contains traces of chlorinated compounds, which are particularly objectionable, since they have an irritating odour, and cause soaps perfumed with the impure substance to deteriorate and darken on exposure to light. Benzaldehyde can, however, be obtained quite free from such impurities, and soap scented with it does not change colour on exposure. As a perfume, artificial benzaldehyde is inferior to the natural oil of almonds.

Benzaldehyde is employed largely for the production of various synthetic products, such as Malachite Green, cinnamic aldehyde, etc.

Reactions.—On exposure to the light, benzaldehyde absorbs oxygen rapidly, and is converted into a crystalline mass of benzoic acid, $C_7H_6O_2$.[2] (Cf. Baeyer and Villiger, *Ber.*, 1900, **33**, 1569.) It is also oxidised by boiling with chromic acid mixture, or manganese dioxide and sulphuric acid; but is only slowly attacked by nitric acid, even when boiling.

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[1] The solubility of benzaldehyde in water is often erroneously stated as 1 in 30, which is 10 times the true amount.

[2] The oxidation is much retarded by the presence of hydrocyanic acid, which is therefore often added to the artificial oil of bitter almonds.

When heated with solid sodium hydroxide, benzaldehyde evolves hydrogen and yields a benzoate. By treatment with water and sodium amalgam, it is reduced to benzyl alcohol. Benzyl alcohol and a benzoate are also formed when benzaldehyde is treated with strong sodium hydroxide solution.

Like most aldehydes, benzaldehyde forms crystalline compounds with alkali hydrogen sulphites. The sodium compound has the formula $C_7H_6O.NaHSO_3$.[1] Benzaldehyde also responds to the other general reactions of aromatic aldehydes. It reduces ammoniacal silver solution with the production of the usual silver mirror, but differs from aldehydes of the aliphatic series in being permanent in presence of alkalies and in not reducing Fehling's solution. Ammonium hydroxide converts benzaldehyde into white crystalline *hydrobenzamide*, $(C_6H_5.CH)_3N_2$, melting at 110°, which is resolved by acids into ammonia and benzaldehyde. This reaction also distinguishes the aromatic aldehydes from those of the fatty series.

Estimation. Volumetric Methods.—Ripper has devised a general method for the estimation of aldehydes and those ketones which combine with sodium hydrogen sulphite (*Monatsh.*, 1901, **21**, 1079). The aldehyde or ketone is absorbed (after steam distillation if necessary) in excess of sodium hydrogen sulphite solution and the excess determined by titration with standard iodine solution. In the experience of the present writer, however, the excess of sulphite found after the absorption of benzaldehyde, varies with the concentration of the solution, and, consequently, appreciable errors are introduced by variation of the duration of the steam distillation, when this is necessary.

Dodge states (Eighth Inter. Cong. App. Chem., Sect. VIII b. Orig. Comm. 17, 15) that benzaldehyde can be estimated by the following modification of Ripper's method. 0.15 grm. of the aldehyde is mixed in a flask with 25 c.c. of N/5 sodium hydrogen sulphite solution and dissolved by gentle shaking. The flask is corked and kept in ice-water for 1.5 to 2 hours. The solution is then titrated cold with N/10 iodine solution using starch as an indicator. The aldehyde can also be estimated by allowing about 1 grm. to stand at room temperature with 10 c.c. of 2.5 N-alcoholic potassium hydroxide solution for 24 hours and then titrating the free alkali. But oil of bitter almonds cannot be analysed by this method.

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[1] This insoluble crystalline compound is converted, in the presence of an excess of sodium hydrogen sulphite, into a soluble compound of the formula $C_7H_5NaSO_3$.

Gravimetric Methods.—For the estimation of small quantities of benzaldehyde Hèrissey (*J. Pharm. Chim.*, 1906, [vi], **23**, 60) converts the aldehyde into its phenylhydrazone. The reaction is not complete at the ordinary temperature in 24 hours, and longer periods give too high results, owing to oxidation of the excess of phenylhydrazine. The following method, however, is stated to give good results: 50 c.c. of the aqueous solution of benzaldehyde are mixed with 50 c.c. of a reagent prepared by dissolving 0.5 c.c. of acetic acid and 1 c.c. of freshly distilled phenylhydrazine in 100 c.c. of water. The mixture is heated on a water-bath for 20 to 30 minutes and then allowed to stand for 12 hours. The precipitate is collected in a tared Gooch crucible, washed with 20 c.c. of cold water, and dried to constant weight over sulphuric acid *in vacuo*. Denis and Dunbar (*J. Ind. Eng. Chem.*, 1909, **1**, 256) employ a similar method for the analysis of almond-flavouring extracts, but as they allow the mixture of extract and phenyl hydrazine to stand 24 hours without heating, their results are somewhat low.

The method described by Denis and Dunbar has been studied both by Smith and by Woodman and Davis. Smith dealt with the application of the method to maraschino products. He found (*U. S. Dept. Agr., Bur. Chem.*, Bull. 152, 192) that distillation in an atmosphere of carbon dioxide gave somewhat better results than in air, whilst distillation from strong sodium chloride solution gave results which were too high. Also that it is best to keep the volume of the solution during precipitation as small as possible, that the results were not affected by the presence of 20% of alcohol (by volume) and that larger amounts may be removed by distillation without affecting the estimation. The precipitate was filtered on two superimposed filter papers, one of which had been counterbalanced against the other, and was again used as a counterpoise after drying. The mean amount of benzaldehyde recovered was 88%.

Woodman and Davis (*J. Ind. Eng. Chem.*, 1912, **4**, 588) state that to obtain accurate results by the Denis and Dunbar method with small quantities the volume of the solution should not exceed 110 c.c. and the alcohol content should be between 8 and 12% by volume. According to these authors the method is not suitable for such small quantities of benzaldehyde as are present in maraschino cherries, for which they recommend a modified method. 100 c.c. of the liquor from maraschino cherries or 50 c.c. of maraschino liqueur, are diluted to 140 c.c. and 110 c.c. distilled off. After approximately determining the alcohol content in a small portion of the distillate 100 c.c. are mixed with alcohol or water sufficient to bring the alcohol content to about 10% by volume. The solution is then shaken vigorously for 10 minutes in a rubber-stoppered flask with 100 c.c. of the freshly prepared phenylhydrazine reagent (3 c.c. of glacial acetic acid mixed well with 40 c.c. of water and 2 c.c. of phenylhydrazine and filtered through several thicknesses of filter paper). The precipitate is collected in a tared Gooch crucible, washed first with cold water and then with 10 c.c. of 10% alcohol and dried either in a vacuum desiccator at 20 cm. pressure for 20–24 hours or in a vacuum oven at 70°–80° for 3 hours. The weight of precipitate obtained in a blank determination is deducted and the corrected weight multiplied by 0.5411 to obtain the weight of benzaldehyde. The method can be applied to almond extracts by using 10 c.c. of the extract diluted to 100 c.c., and 15 c.c. of the reagent. In maraschino cherries the benzaldehyde expressed in mg. per 100 c.c. of the liquor should not be more than two or three times the alcohol content expressed in percentage by volume.

G. A. Geiger has elaborated (*J. Amer. Chem. Soc.*, 1918, **40**, 1453–1456) an accurate, though somewhat slow, method of estimating benzoic acid and benzaldehyde when present together. The solution containing not more than 0.5 grm. of benzaldehyde and benzoic acid is made distinctly alkaline with sodium hydroxide and extracted with three quantities of 25 c.c. of ether; the combined etheral extracts are treated with 1.5 grm. of freshly-distilled phenylhydrazine and 10 c.c. of a 10% solution of acetic acid in ether. The solution is evaporated in a current of air, the residue mixed with 50 c.c. of water and the insoluble benzylidenephenylhydrazone collected in a tared Gooch crucible, dried for 2 hours at 70° in a vacuum, and weighed. The solution from which the benzaldehyde has been extracted is rendered slightly acid with hydrochloric acid (1:3) extracted with 25 c.c. of chloroform, saturated with salt and extracted three times with 25 c.c. of chloroform. The chloroform is evaporated at ordinary temperature, and the residue dissolved in neutral 50% alcohol and titrated with sodium hydroxide. If the ethereal solution of benzaldehyde is washed with 25 c.c. of N/5 sodium hydroxide solution the quantity of benzoic acid separated is larger and the accuracy of the method is increased.

According to Golse (*J. Pharm. Chim.*, 1915, **12**, 44) the French official method of estimating hydrocyanic acid and benzaldehyde in liqueurs is untrustworthy, the chief objections being the use of insufficient alkali to fix the hydrocyanic acid and faulty conditions of precipitation of the aldehyde phenylhydrazone. The author recommends the following procedure: 200 c.c. of the liqueur are treated with 1 c.c. of sodium hydroxide solution (sp. gr. 1.32–1.36) in a 600 c.c. flask and distilled until 175 c.c. of distillate have been collected (*A*). The residual liquid in the flask is then cooled, 50 c.c. of 10% sulphuric acid solution are added slowly from a tap-funnel and the mixture again distilled 50 c.c. of distillate being collected in a receiver containing 5 c.c. of ammonia (*B*). The distillate (*A*) is now transferred to a distillation flask, 5 c.c. of the phenylhydrazine reagent added, the mixture diluted to 200 c.c., and 75 c.c. distilled over; this distillate contains traces of hydrocyanic acid and is added to the distillate (*B*). The lower end of the condenser is then closed and the flask heated on a water-bath until the hydrazone has been precipitated, 2 hours heating being usually sufficient. The precipitate is collected on a filter paper, washed with water and dissolved by treatment with 10 c.c. of alcohol followed by 20 c.c. of ether. The alcohol-ether solution is evaporated, the residue dried in *vacuo* and weighed. The weight × 2.7 gives the weight of benzaldehyde in a litre of the liqueur. The phenylhydrazine reagent is prepared by dissolving 1 grm. of phenylhydrazine in a mixture of 4 c.c. of glacial acetic acid, 2 grm. of sodium acetate and 20 c.c. of water, heating and shaking vigorously, adding 1 c.c. of sodium hydrogen sulphite solution and filtering. The presence of the sodium hydrogen sulphite prevents the oxidation of the phenylhydrazone during precipitation.

The distillate (*B*) is used for the estimation of the hydrocyanic acid.

Feinberg (*Eighth Int. Cong. Appl. Chem.*, 1912, Sect. 1, Orig. Comm. **1**, 187) has made an investigation of the methods of estimating typical aldehydes, and publishes results which show that for benzaldehyde the neutral sulphite method is better than that with bisulphite, and that precipitation with *p*-nitrophenylhydrazine gives better results than using *p*-bromophenylhydrazine, the neutral sulphite method being perhaps slightly less accurate than precipitation with *p*-nitrophenylhydrazine. The best results are stated to be obtained as follows: 25 c.c. of a 1% solution of the aldehyde in 12% acetic acid are diluted with 50 c.c. of water, and a solution of twice the theoretical quantity of *p*-nitrophenylhydrazine in 30 c.c. of 30% acetic acid is added. After standing for 5 hours the precipitate is collected on a tared Gooch crucible, washed with 10% acetic acid until the washings no longer give a strong colour with dilute alkali, dried at 105°-110° and weighed. When the benzoic acid present is separately determined by titration with standard alkali solution and deducted from the weight of aldehyde (calculated from that of the hydrazone by multiplying by 0.4400) results showing an accuracy of 99% are obtained.

Hoffmeister has described (*Arb. Pharm. Inst. Univ. Berlin*, 1913, 10, 147) methods of estimating benzaldehyde in essential oils which depend on the removal of the aldehyde with sodium bisulphite, decomposition of the bisulphite compound with sodium hydroxide solution and subsequent precipitation of the aldehyde with phenylhydrazine.

Colorimetric Method.—Woodman and Lyford have based a method of estimating benzaldehyde in almond extracts on the colour reaction of aldehydes with magenta decolorised by sulphur dioxide. (*J. Amer. Chem. Soc.*, 1908, 30, 1607.)

This has the advantage of being considerably more rapid than the gravimetric method. The reagent is prepared by dissolving 0.5 grm. of magenta in 100 c.c. of water, adding a solution of 20 grm. of sulphur dioxide and diluting to 1 litre. 3 standard solutions are prepared by dissolving, respectively, 0.002 grm., 0.004 grm., and 0.006 grm. of freshly distilled benzaldehyde in aldehyde-free alcohol and diluting to 20 c.c. 10 grm. of the sample to be analysed are diluted to 50 c.c. with alcohol (aldehyde-free), and of this solution 2 c.c. are diluted to 20 c.c. with the same solvent. The latter solution and the 3 standards, contained in Nessler tubes, are immersed for some time in water at 15°, then each is treated rapidly with 20 c.c. of the magenta reagent (also at 15°) and well mixed. After standing for 10 minutes the test sample is matched with the nearest standard in the usual way by withdrawing part of either liquid. The depth of colour, within the given limits, is proportional to the amount of benzaldehyde present. To prepare aldehyde-free alcohol it is distilled over silver oxide, then treated with 25 grm. of *m*-phenylenediamine hydrochloride per litre, and a rapid current of air passed through the solution for 3 hours. The liquid is then distilled, the first 100 c.c. being rejected. Alcohol so treated remains pure for some weeks if kept in the dark at a low temperature.

ESSENTIAL OIL OF BITTER ALMONDS

The essential oil of bitter almonds, *Amygdalus communis* var. *amara*, together with the oils of several other kernels, such as those of the apricot and peach, owe their characteristic odour and flavour to benzaldehyde.[1] To all intents and purposes the oils from these 3 sources are identical, and most of the foreign bitter-almond oil is in reality peach-kernel oil.

Lewkowitsch states (*Analyst*, 1904, **29**, 105) that the oil sold as "Oil of sweet almonds, French" is solely peach-kernel or apricot-kernel oil, whilst "Almond-oil, English" is genuine.

The oil does not exist in the free state in the kernels, but results from the decomposition of a glucoside, *amygdalin*, $C_{20}H_{27}NO_{11}$, which breaks down in the presence of water under the influence of the natural enzyme *emulsin* or *synaptase* into a mixture of dextrose, benzaldehyde and hydrocyanic acid.

This reaction is also brought about by the action of dilute hydrochloric acid.

Pure oil of bitter almonds contains much hydrocyanic acid (*vide infra*), but the acid-free oil is a regular commercial article, sold as "Oil of Almonds, S. A. P." (*sine acido prussico*).

Approximately from 1 to 2% of essential oil is obtained from the bitter-almond kernels, and this possesses a much finer and more delicate odour than synthetic benzaldehyde. Bitter-almond oil is a yellowish liquid (which can be obtained colourless by rectification) of sp. gr. 1.045 to 1.070. The latter gravity is, however, somewhat rare, and normal oils seldom range outside the limits 1.045 and 1.060.

M. Boyveau states that an artificial oil of bitter almonds is occasionally met with having a sp. gr. of 1.029 to 1.030. Its odour is more acrid than that of the natural oil, as may be observed by moistening strips of paper with the oil and exposing them to the air.

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[1] According to Tilden, cherry-laurel oil consists of benzaldehyde, less than 2 % of hydrocyanic acid, a volatile oil (possibly benzyl alcohol), convertible into benzoic acid by oxidation, and minute quantities of an odorous resin (*Pharm. J.*, 1875, (iii), **5**, 761).

Oil of bitter almonds is optically inactive, and neutral to ordinary indicators when fresh. On exposure to light it rapidly absorbs oxygen and deposits crystals of benzoic acid, at the same time becoming acid in reaction.

The main constituent of essential oil of bitter almonds is benzaldehyde, but a notable proportion of hydrocyanic acid (4 to 8%) is present, and appreciable quantities of phenyl-hydroxyacetonitrile (the nitrile of mandelic acid), $C_6H_5.CH(OH).CN$.[1] This last-named substance, also known as benzaldehyde-cyanohydrin, is formed by a direct combination of benzaldehyde and hydrocyanic acid.

Mandelo-nitrile has a sp. gr. of 1.124, and is easily decomposable. Hence normal almond oils containing from 1.5 to 4% of hydrocyanic acid have a sp. gr. usually falling between the limits of 1.052 and 1.058. Oils containing a larger quantity of hydrocyanic acid, even up to 11%, have been known to reach the very abnormal sp. gr. of 1.096.[2]

When oil of bitter almonds is fractionally distilled, hydrocyanic acid passes over first, and then tolerably pure benzaldehyde.

Oil of bitter almonds may be deprived of its hydrocyanic acid in several ways. Treatment with water, mercuric oxide, lime, and ferrous chloride has been recommended. Mackay treats the oil for 48 hours with lime and a solution of potassium hydroxide.

Bitter-almond oil is stated to give a crimson coloration with strong sulphuric acid, becoming brownish on exposure to the air. If the crimson liquid be poured into water the red colour disappears, and a yellow precipitate is produced, which sometimes takes the form of globules.

Essential oil of peach kernels is frequently sold as oil of bitter almonds, but the most common falsification is synthetic benzaldehyde.

Chwolles states (*Chem. Zeit.*, 1903, **27**, 33) that the phloroglucinol reaction of peach-kernel oil, described by Kreis (*Chem. Zeit.*, 1902, **26**, 897, 1014) is not given by almond oil. But Lewkowitsch (*loc. cit.*) records the occurrence of genuine almond oils which do not differ from peach-kernel oil in this respect. According to this author, the only test which will differentiate almond oil from apricot-kernel and peach-kernel oils is Bieber's test. In this 5 c.c. of the oil are treated with 1 c.c. of a mixture of equal weights of sulphuric and fuming nitric acids. Peach-kernel oil gives a peach-blossom tint, apricot-kernel oil gives a pink colour, whilst almond oil remains colourless. Admixture of 33% of apricot-kernel oil can be recognised by this means. The reaction is not so marked when the oils have been kept, and the nitro-sulphuric reagent must be fresh. Cf. Vol. 2, p. 135.

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[1] Benzoin, $C_6H_5.CH(OH).CO.C_6H_5$, is stated to be present in some specimens of bitter-almond oil. It is a solid camphor-like substance melting at 137°, and occurs most largely in samples of oil of high density, in the preparation or purification of which a high temperature has been employed. It gives a purple colour with strong sulphuric acid.

[2] Schimmel & Co., (*Report*, April, 1893) added a 20 % solution of hydrocyanic acid to a sample of bitter-almond oil which had a sp. gr. of 1.054. In two days the sp. gr. had risen to 1.074. It is thus clear that bitter-almond oils of high gravity contain comparatively large proportions of mandelo-nitrile.

To distinguish the natural from the artificial product, Boyveau shakes 1 c.c. of the oil with 1 c.c. of concentrated sulphuric acid. The *natural oil* becomes currant-red, deepening in a few hours to a more intense and darker red, the mixture remaining perfectly clear. *Cherry-laurel* immediately takes a dark red tint, without first passing through the delicate currant-red shade observed with bitter-almond oil. The mixture thickens somewhat, but remains perfectly fluid and clear. The oils from *peach*, and *apricot-kernels* behave somewhat similarly, but give an evanescent currant-red tint, changing to a very dark red. *Artificial almond oil* first takes a red tint, and then immediately becomes brown, loses its transparency, and thickens, becoming a solid brownish mass in the course of 24 hours. By the loss of transparency and production of the brown colour an admixture of 25% of the artificial oil in the natural oil of bitter almonds is said to be recognisable.

Synthetic benzaldehyde, as already stated, usually contains marked traces of organic chlorine compounds. Some commercial specimens are free from these impurities and command a far higher price.

Analysis of Benzaldehyde

The method of analysis adopted by the U. S. Pharmacopœia 8th Rev. is replaced in the 9th Rev. (1916) edition by the following:

Dissolve about 3 c.c. of freshly distilled phenylhydrazine in 60 c.c. of alcohol and titrate 25 c.c. of the solution, which must always be freshly prepared, with N/2 hydrogen chloride solution using methyl orange as indicator. To about 1 grm. of benzaldehyde, accurately weighed, add 25 c.c. of the phenylhydrazine solution just prepared and allow it to stand for 30 minutes. Add a drop of methyl orange solution and acidify the mixture by adding a measured excess of N/2 hydrogen chloride solution. Filter the mixture and wash the precipitate with small quantities of water until the washings cease to redden blue litmus paper. Then titrate the excess of hydrogen chloride in the filtrate and washings with N/2 potassium hydroxide solution. Subtract the number of c.c. of N/2 hydrogen chloride solution consumed from the number of c.c. of the same solution used in titrating the 25 c.c. of phenylhydrazine solution; the difference multiplied by 0.053 gives the weight of the benzaldehyde present.

According to the standard set by the U. S. Pharmacopœia 1916 benzaldehyde must give the following tests.

When ten drops of the aldehyde are treated with 5 c.c. of water 0.5 c.c. of potassium hydroxide solution (5%) and 0.1 grm. of ferrous sulphate, warmed gently and then acidified with hydrochloric acid, no greenish blue colour or blue precipitate should be produced within 15 minutes (absence of hydrogen cyanide).

No halogen should be detectable by the ignited copper wire test.

When 1 c.c. of the aldehyde is dissolved in 20 c.c. of alcohol, sufficient water added to produce a slight turbidity, a brisk evolution of hydrogen maintained in the solution for 1 hour by addition of zinc and diluted sulphuric acid and the liquid filtered and evaporated to about 20 c.c., then 10 c.c. of the concentrated liquid should not give a violet colour when boiled with a drop of potassium dichromate solution (absence of nitrobenzene).

Chlorine.

According to M. S. Salaman (*Perf. and Essent. Oil Rec.*, 1917, **8**, 41–42) the following simple way of estimating chlorine in benzaldehyde gives results only very slightly lower than those obtained by the Carius method. About 1 grm. of the sample of benzaldehyde is heated in a retort with 40 c.c. of sulphuric acid and 5 c.c. of strong nitric acid. The heating must be very gradual and the mixture should not be allowed to froth until the end of the operation. The fumes are collected in a solution of silver nitrate and heating is continued until no further precipitate is produced, which will require somewhat less than 3 hours. The silver solution is then acidified with nitric acid, boiled to decompose any sulphite, and the chloride is determined in the usual way.

J. Voigt has described (*Z. angew. Chem.*, 1922, **35**, 654–655) an apparatus for the accurate estimation of traces of chlorine in volatile organic compounds, particularly in synthetic benzaldehyde. 10 to 20 grm. of the aldehyde are weighed into a lamp composed of a glass bulb arranged horizontally in an air-bath which can be heated, and connected with a combustion-tube shaped like a pipette. Hydrogen is passed through the lamp and carries over the benzaldehyde vapours; the outlet tube projects into the bulb of the combustion tube and ends in a burner nozzle formed by a quartz capillary. The issuing hydrogen and benzaldehyde are ignited and burn quietly in oxygen supplied to the combustion tube till all the aldehyde has been volatilised. The products of combustion are passed over 2–3 grm. of granular anhydrous sodium carbonate packed in the narrow part of the combustion tube and heated by gas burners, and the water formed is collected in a vessel containing calcium chloride. About 7 grm. of benzaldehyde can be burned per hour. At the end of the combustion the soda is washed out into a beaker with dilute nitric acid and titrated with N/10 silver nitrate solution. As little as 0.001% of halogen can be accurately estimated by this method, and it is important to apply a correction for the chlorine which is always present in the hydrogen employed as, although undetectable by ordinary methods, the amount may make an appreciable difference in the present case. Hydrogen in cylinders contains on the average 0.003 grm. of chlorine per cubic metre.

A somewhat similar method has been described by Schimmel (*Ber.* von Schimmel & Co., 1921, 56–61).

Both Herzog (*Ber. Pharm. Ges.*, 1911, **21**, 536) and Heyl (*Apoth. Zeit.* 1912, **27**, 49) adversely criticise the method of the German Pharmacopœia, 5th Edition, for the detection of chlorine compounds in benzaldehyde. Heyl recommends instead that 10–15 drops should be mixed with 1–2 grm. of pure slaked lime, the mixture covered with a thin layer of lime and the whole ignited to redness. The residue is taken up with 5–6 c.c. of water, dissolved in nitric acid and tested with silver nitrate solution. 1 drop of monochlorobenzene, it is stated, can be detected in 50 grm. of benzaldehyde in this way.

Lunge (*Chemische-Technische Untersuchungs Methoden*, Vol.3, page 807 [1905]) recommends the following methods for detecting benzyl chloride and chlorobenzaldehyde.

Benzyl Chloride.—10 grm. of the sample are distilled and the first 10 to 12 drops of the distillate collected in alcoholic potassium hydroxide solution (5%). This solution is boiled for some time in a reflux apparatus and then evaporated to dryness. The residue is dissolved in water, any oil remaining extracted with ether, and the aqueous solution treated with nitric acid. The precipitated benzoic acid is filtered off, and the filtrate tested with silver nitrate.

Chlorobenzaldehyde.—2 c.c. of the oil are shaken with a solution of 6 grm. of sodium carbonate in 40 c.c. of water, the liquid gently warmed and treated gradually with a 5% solution of potassium permanganate until a faint pink tint is permanently formed. The excess of permanganate is then destroyed by addition of alcohol drop by drop. The liquid is filtered, acidified with dilute sulphuric acid, well cooled and the precipitated benzoic acid collected. This is washed with cold water, dissolved in sodium carbonate solution containing potassium nitrate, and the liquid evaporated to dryness. The residue after ignition is dissolved in dilute nitric acid and tested with silver nitrate solution. The occurrence of organic chlorine compounds in oil of bitter almonds may be regarded as very strong evidence of adulteration with synthetic benzaldehyde.

Hydrocyanic acid may be detected in bitter-almond oil by agitating the sample with water, and applying tests to the latter. Ferric chloride and ferrous chloride or sulphate should be added, and then a solution of sodium hydroxide. On acidifying the liquid with hydrochloric acid, a bluish-green coloration or prussian-blue precipitate will be formed if hydrocyanic acid was present. An aliquot part of the aqueous solution may be employed for quantitative estimation by precipitation or titration with silver nitrate.

A preferable method is to dissolve 1 grm. of the oil in 5 c.c. of alcohol and dilute with water to 50 c.c. Excess of ammonio-silver nitrate is then added, and the mixture well agitated for a few minutes. The solution is then slightly acidified with nitric acid, and the precipitated silver cyanide collected, washed, dried, and weighed, or ignited in the air and the resultant metallic silver weighed. 5 parts (nearly) of silver cyanide or 4 of metallic silver correspond to one of hydrocyanic acid.

Occasionally *alcohol* is added, but this is not always done with a fraudulent intention, as it is believed to retard oxidation.

Alcohol reduces the density of bitter-almond oil.

According to Lunge, it is best detected by shaking the oil in a graduated cylinder with an equal volume of a saturated solution of calcium chloride. The presence of alcohol and approximately its amount will be indicated by a decrease in volume of the oil.

Nitrobenzene, $C_6H_5NO_2$, is sometimes used as an adulterant of bitter-almond oil, and has even been sold as a substitute under the name of "artificial essence of bitter almonds." Nitrobenzene has a density of 1.186, and hence is heavier than bitter-almond oil, from which it also differs in not yielding benzoic acid when a current of air is passed through it. It is an insidious poison, and should be rigidly excluded from articles of food.

The following method may be employed for the detection and approximate estimation of nitrobenzene in bitter-almond oil. Some clean sand or emery is introduced into a wide-mouthed flask, and a known weight (about 1 grm.) of the sample to be tested, added. This is followed by 40 c.c. of a saturated aqueous solution of sodium hydrogen sulphite, the whole agitated briskly for a few minutes, and then shaken with ether free from alcohol. The benzaldehyde forms a compound with the sulphite, whilst any nitrobenzene dissolves in the ether. The upper layer is withdrawn by a pipette, more ether added, and the agitation repeated. The ether is again withdrawn by means of the pipette, the united liquids evaporated at a gentle heat, and the residual nitrobenzene weighed. The method is only roughly approximate. If the quantity of nitrobenzene be small or there be any doubt as to its identity, 4 or 5 drops of the sample should be dissolved in alcohol and heated for some time with hydrochloric acid and granulated zinc. The nascent hydrogen reduces the nitrobenzene to aniline, C_6H_7N. The liquid is filtered through wet paper, rendered alkaline with a solution of sodium hydroxide,[1] agitated with ether, and the ethereal layer removed and shaken with water and a few drops of dilute hydrochloric acid. The ether is separated, and a dilute solution of bleaching powder is cautiously added to the aqueous liquid, when if nitrobenzene were originally present, a violet colour (mauve) will be developed. The process requires to be skilfully conducted. Reduction to aniline may be conveniently used for distinguishing bitter-almond oil from nitrobenzene, but not for detecting the latter in presence of the former. When this is required, the sulphite and ether process must be previously used for their separation.[2]

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[1] When the nitrobenzene occurs in quantity, bleaching powder may be added at once to the filtered liquid after nearly neutralising it with alkali.

[2] Most other essential oils can also be separated from benzaldehyde by means of sodium-hydrogen sulphite and ether.

The following method for detecting and approximately estimating nitrobenzene in bitter-almond oil is due to Maisch. 1 c.c. of the sample is dissolved in 12 c.c. of absolute alcohol, and 0.75 grm. of fused potassium hydroxide added. The liquid is boiled till it is reduced to about 4 c.c., and left to cool. If the sample be pure no crystals form, but a brown colour is slowly developed. The residual liquid is entirely soluble in water. In the presence of nitrobenzene, brown crystals of azo-oxybenzene, $C_{12}H_{10}N_2O$, are formed, which are insoluble in water, and may be collected, dried by pressure, and weighed.

Mapurgo (*Pharm. Zeit. Russ.*, 1890, **29**, 205) detects nitrobenzne by the following test: 2 drops of phenol, 3 drops of water, and a fragment of potassium hydroxide the size of a pea are heated to boiling in a small basin, added to a little of the oil mixed with water, and the mixture boiled. The formation, at the conclusion of the heating, of a crimson-red ring at the surface of the liquid changed to emerald-green by adding calcium chloride solution indicates the presence of nitrobenzene.

P. Hasse (*Chem. Zeit.*, 1922, **46**, 234) detects nitrobenzene in benzaldehyde by adding 0.2 grm. of sodium hydrogen sulphite to a few drops of the sample contained in a test-tube half filled with water and shaking the mixture. The odour of benzaldehyde disappears, but that of nitrobenzene persists, if this compound is present. If sulphur dioxide is evolved, normal sodium sulphite may be used to absorb it.

According to A. Reclaire (*Perf. and Essent. Oil Rec.*, 1922, **13**, 356), Hasse's method of detecting nitrobenzene is only reliable if 10% is present, whilst the pink to red coloration with a very dilute alcoholic solution of sodium hydroxide described by Pickering (*Chem. Trade J.*, 1922, **70**, 144) as characteristic of nitrobenzene is not a reaction of this substance at all, but of dinitrothiophene, which is often present in commercial nitrobenzene. The method of Pinoff (*Pharm. Zentralh.*, 1921, **62**, 610) depending on the formation by formaldehyde-ammonia of an emulsion with benzaldehyde, but not with nitrobenzene, does not appear satisfactory, as no difference could be observed with mixtures containing 1–10% of nitrobenzene.

Benzoic acid is always present, 1 to 3% being not unusual in the best commercial products. It may be estimated by dissolving 10 grm. of the oil in 50 c.c. of alcohol and titrating the solution with N-sodium hydroxide solution, using phenolphthalein as indicator.

According to the United States Pharmacopœia, oil of bitter almonds must contain 85% of benzaldehyde and not more than 4% nor less than 2% of hydrocyanic acid.

Essence of bitter almonds is the name given to a solution of commercial oil of bitter almonds in different proportions of rectified spirit. It is employed as a flavouring agent, for which purpose it should be quite free from hydrocyanic acid. *Almond flavour* is a solution of one part of the oil in 7 of rectified spirit. The proportion of alcohol in these preparations is best estimated by fractional distillation.

Bitter-almond water is a solution of bitter-almond oil in water. Fromm states (*Apoth. Zeit.*, 1897, **12**, 254) that artificial bitter-almond water consists of hydrocyanic acid, benzaldehyde, mandelonitrile, water, and alcohol, whilst the natural product contains in addition small quantities of ammonia and of substances having a peculiar odour, possibly amino-compounds. To distinguish the artificial from the natural product, 10 c.c. are treated with 20 c.c. of hydrogen peroxide solution (free from hydrogen chloride), then warmed with 2 to 5 grm. of sodium hydroxide until the odour of benzaldehyde disappears, and evaporated to dryness. The residue is gently ignited, dissolved in nitric acid and the solution tested with silver nitrate. Chlorine is present in the artificial, but not in the natural substance. It is not a preparation of the British Pharmacopœia, but is official in several other countries. Its strength is uncertain. The proportion of hydrocyanic acid it contains may be estimated with silver nitrate after adding sufficient magnesium hydroxide to leave the sample slightly opalescent. The mixture should be left at rest for half an hour and then titrated with decinormal silver nitrate, neutral potassium chromate being used as an indicator. Basic magnesium acetate is said to be preferable to magnesium hydroxide (Beckurts, *Pharm. Central.*, 1887, **8**, 131; Linde, *Arch. Pharm.*, 1887, [iii], **25**, 690). Bitter-almond water should retain its characteristic odour after the removal of all the hydrocyanic acid by the above process or by agitation with excess of silver nitrate.

To test for excess of hydrocyanic acid in bitter-almond water, 10 c.c. should be treated with 1 c.c. of decinormal silver nitrate and a few drops of nitric acid, and filtered. The filtrate should give no immediate precipitate on addition of more silver nitrate.

Cherry-laurel water (*Aqua lauro-cerasi*, British Pharmacopœia), prepared by distilling fresh cherry-laurel leaves with water, and **Cherry water,** from wild cherries, are preparations very similar to bitter-almond water; but the last-named becomes milky immediately on addition of ammonia, which is the effect not produced on laurel water till after a lapse of some time.

The British Pharmacopœia requires cherry-laurel water to contain 0.10% of HCN, when assayed by titration with standard silver nitrate solution.

Acetophenone. Phenyl-methylketone, $C_6H_5.CO.CH_3$.

This substance results from the action of benzoyl chloride on zinc-methyl or by distilling a mixture of calcium benzoate and acetate (Friedel, *J.*, 1857, 270). It may also be readily prepared by the interaction of benzene and acetyl chloride in the presence of aluminium chloride (Friedel and Crafts, *Ann. Chim. Phys.*, 1886, [vi], **1,** 507). The 2 last-named methods are those usually adopted on the manufacturing scale.

Acetophenone crystallises in large laminæ, melting at 20° to a colourless, mobile liquid of about the density of water, boiling at 202°. It has a very persistent odour, recalling that of bitter-almond and cherry-laurel water. It is nearly insoluble in water, soluble in 60 parts of glycerol and very soluble in alcohol, ether, chloroform, petroleum spirit, and fatty oils. Dissolved in fixed oil of almonds, it is frequently administered in gelatin capsules.

Reactions.—Acetophenone is neutral and gives no coloration or characteristic reaction with ferric chloride, hydrochloric acid, or sulphuric acid. By oxidation with chromic acid mixture it is converted into benzoic and carbonic acids. With nitric acid it gives a yellow coloration.

Acetophenone has hypnotic properties, and has been introduced into medicine under the name of "hypnone" (*Pharm. J.*, 1886, [iii], **16,** 445, 582).

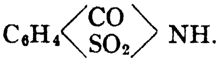
Estimation.—According to Marsh and Struthers (*Proc.*, 1908, **24,** 267), acetophenone reacts with mercuric iodide, dissolved in cold aqueous potassium hydroxide, as shown by the equation

$$PhCOMe + 6HgI_2 + 4KOH = HgI, PhCO.CHg_3I_3 + 2K_2HgI_4 + 4H_2O$$

the ketone compound being a yellow precipitate. In the absence of other ketones, therefore, acetophenone may be estimated either by determining volumetrically the amount of alkali absorbed in the presence of excess of mercuric iodide, or by weighing the precipitate formed.

Gallacetophenone. $CH_3.CO.C_6H_2(OH)_3$. This substance, also known as *trihydroxyacetophenone* and as "Alizarin Yellow C," may be regarded as a trihydroxy derivative of acetophenone or as a methylketo-compound of pyrogallic acid. It is a yellow powder, melting at 168°, and is soluble in warm water, alcohol, ether, and glycerol. It is only very slightly soluble in cold water, but more so in solution of sodium acetate. It is used (in the form of an ointment) to a certain extent as a remedy for psoriasis, being a substitute for pyrogallol.

Saccharin:



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH.$$

1–2-*sulphaminbenzoic anhydride; o-benzoicsulphinide; Benzosulphinidum* (United States Pharmacopœia, viii); *Glusidum* (British Pharmacopœia).

Saccharin is prepared by sulphonating toluene, converting the mixed sulphonic acids into the sulphochlorides, separating the *o*-isomeride, converting this into the amide, and oxidising the latter with potassium permanganate. (Fahlberg and Remsen, *Ber.*, 1879, **12**, 469; Fahlberg and List, *Ber.*, 1887, **20**, 1597; von Heyden, D. R. P. 85491; Bayer & Co., D. R. P. 96125.)

The crude material is often contaminated with by-products, among which is 1–4-sulphaminobenzoic acid. Numerous methods for the purification of the saccharin have been proposed, among which are the following:

A. R. Ling (*Br. pat.*, 1893, 21417) proposes treatment of the crude product with a solution of sodium acetate. The saccharin passes into solution as a sodium compound; the 1:4 compound remains undissolved.

F. von Heyden (*Br. pat.*, 1893, 10769), by crystallisation of the solution containing the mixed salts (potassium, sodium, calcium, or magnesium) of the 2 forms, by which the 1:4 salt remains in solution, being much more soluble than the 1:2: form.

Saccharin is a white crystalline powder, with a faintly aromatic odour and intense, sweet taste; 1 part in 10,000 of water can be detected by the taste. It melts at 220°. Its solubilities are; 1 part dissolves in 400 parts of cold water, 100 parts of boiling water, 25 parts of (90%) alcohol, and 120 parts of ether. It is also soluble in a mixture of ether and petroleum spirit. These immiscible solvents extract it from an (acidified) solution in water. It is soluble in glycerol. Water containing alkali or alkali carbonates dissolves more than pure water. As already noted, the hydrogen atom of the imino-group may be replaced by other positive radicals. Some of these derivatives are more soluble than saccharin itself and have more or less of its sweetness.

Sodium saccharin, $C_6H_4(CO)(SO_2)NNa + 2H_2O$, occurs in commerce under the name of "soluble saccharin" or "crystallose." It separates from hot water in readily soluble crystals.

COMMERCIAL SACCHARIN

Apart from the by-products of manufacture, saccharin is liable to adulteration with diluents both organic and inorganic. Samples containing little else than inert mineral matter, such as calcium sulphate, have been found. As pure saccharin sublimes entirely at a temperature not much above its m. p., ordinary mineral adulterants are indicated by notable amounts of ash.

The British Pharmacopœia 1914 sets the following standard of purity for saccharin.

> "1 grm. heated for 4 hours on a water-bath with 10 c.c. of a mixture of 4 volumes of sulphuric acid and 3 volumes of water completely dissolves, and when the solution is diluted with an equal volume of water and allowed to stand for 24 hours, no crystals separate. Gently warmed for a short time with sulphuric acid no blackening occurs. Ash not more than 0.5%.

According to the United States Pharmacopœia 1916, saccharin must not contain more than 0.5% of ash, and when a solution of 0.2 grm. of the sample in 10 c.c. of sulphuric acid is kept at 48°–50° it must not develop more than a brown colour within 10 minutes. Further, it must be free from benzoic and salicylic acids and from glucose and lactose. The acids are tested for by adding ferric chloride solution, drop by drop, to 10 c.c. of a hot saturated aqueous solution of saccharin when no precipitate or violet colour should appear. To test for the sugars, a solution of about 0.2 grm. of saccharin in 5 c.c. of potassium hydroxide solution is heated with 10 c.c. of Fehling solution, when no cuprous oxide should be deposited.

Sugars, glucose and starch will be left insoluble after repeatedly treating the solid sample with ether. A better separation from sugar can be obtained by repeatedly agitating the acidified aqueous solution of the sample with ether. If, after removing the ether, the aqueous layer be found, after neutralisation, to have a distinctly sweet taste, the presence of sugar is certain. The quantity can be ascertained by Fehling's solution after inverting the sugar, and preferably after removing the saccharin by ether. Saccharin does not reduce Fehling's solution.

Saccharin should not blacken when treated with cold concentrated sulphuric acid, and even on heating the mixture to 100° for 10 minutes the coloration should merely be faint brown.

Benzoic or salicylic acid can be detected by heating a small amount of the sample with water, allowing the liquid to cool, filtering and testing the filtrate with ferric chloride. Benzoic acid will be shown by a turbidity; salicylic acid by a violet tint.

One of the usual by-products in commercial saccharin is 1–4-sulphaminobenzoic acid, $C_6H_4(COOH)SO_2NH_2$. For the detection of this, 1 grm. of the sample should be shaken with 70 c.c. of ether at 15° for a few minutes, the ether drawn off as far as possible, the undissolved portion dried and its m. p. determined. This should not be above 220°. The amino-acid is much less soluble in ether than saccharin. The amino-acid melts at about 282°.

Langbein (*Zeit. angew. Chem.*, 1896, 486) estimates the amount of *p*-sulphaminobenzoic acid in a sample of commercial saccharin by determining its heat of combustion. Saccharin has the heat of combustion 4753.1 cal. whilst that of *p*-sulphaminobenzoic acid is 4307.3 cal. The method is stated to give good results.

H. D. Richmond and C. A. Hill have published (*J. Soc. Chem. Ind.*, 1918, **37**, 246–249T; 1919, **38**, 8–10T) two noteworthy papers on the estimation of *o*-benzoicsulphinide and of impurities in commercial saccharin. As regards the former these authors conclude (1) that Reid's hydrochloric acid method is accurate but rather troublesome, (2) that Proctor's modification of Reid's method leads to low results; it is insufficiently described and causes discrepancies between analysts. By increasing the time to 4 hours or the strength of the acid to 1.5N it becomes reliable, (3) that the sulphuric acid methods are not so good as the hydrochloric acid hydrolysis; the half-minute process is a very rapid approximate method, but requires to be used with caution. Richmond and Hill recommend the following alkaline-acid hydrolysis, which they state is rapid, convenient and accurate. The saccharin is boiled for 2 minutes with 10 c.c. of 7.5 N sodium hydroxide solution taking care not to concentrate the liquid appreciably, then treated with 50 c.c. of 10 N hydrochloric acid and the boiling continued for 50 minutes (powdered pumice being added if necessary to prevent "bumping") under any form of reflux which condenses efficiently without retaining an appreciable amount of liquid. Sodium chloride should not be deposited whilst the liquid is boiling. After the heating is completed, the liquid is cooled, 75 c.c. of cold water added and a current of air passed through the upper part of the flask to expel any acid vapour. 15 c.c. of 7.5 N sodium hydroxide solution are added carefully and the flask at once connected with a distillation apparatus provided with an efficient steam trap, a condenser and an absorption flask in which are placed 20 c.c. of N/5 hydrogen chloride solution. The distillation is started with a small flame to obviate a considerable rush of air through the standard acid, which would be liable to result in incomplete absorption of the ammonia. After the air has ceased to bubble through the acid the flame is raised and about 70 c.c. are distilled. The distillate is titrated with N/10 alkali using methyl-red as indicator and the result is corrected for a blank test of the reagents. Using 0.6109 grm. of saccharin, the number of c.c. of N/10 acid neutralised multiplied by 3 equals the percentage of *o*-benzoicsulphinide. The method causes a slight hydrolysis of *p*-sulphaminobenzoic acid and of *o*-toluenesulphonamide, but this is negligible in commercial saccharin.

In the estimation of *moisture* by drying in a water-oven, the authors point out that if the saccharin be damp a minute portion may be hydrolysed, resulting in an increase in weight.

In the estimation of the *ash*, advantage should be taken of the volatility of saccharin. The sample is heated gently at first till nearly all the saccharin has sublimed, and then ignited. The solubility in acetone forms a qualitative test. A poor sample gave 3.2% of ash and 3.9% insoluble in acetone.

_p_-Sulphonaminobenzoic Acid.—Richmond and Hill put the limit of sensitiveness of the B. P. test for this acid at 2%. They modify it as follows. 1½ grm. of the saccharin are heated with 10 c.c. of 70.5% sulphuric acid so that the liquid boils as nearly as possible in 1 minute, and boiled for exactly half a minute. The solution is at once poured into 15 c.c. of distilled water kept cool by immersing the vessel in cold water. After mixing, the solution is cooled under the tap, seeded with a trace of the para-acid and placed in ice-water. *p*-Sulphonaminobenzoic acid, if present to the extent of 1%, crystallises out in 30 minutes or less; if 3% is present the crystals usually begin to separate on cooling, before seeding, and when as much as 10% is present the para-acid begins to crystallise from the hot solution. The authors consider this test to be the most rapid and reliable indication of the presence of the para-acid and to be roughly quantitative. They find Remsen and Burton's method approximately accurate only, the results being always low. They believe Proctor's first method—depending on the difference between the benzoylsulphonimide and the total acidity—to be fairly good, but consider his iodide-iodate method of titration much less accurate than direct titration with caustic soda and phenolphthalein; in the former the results vary with the time before titration. With regard to Proctor's second method—extraction of the hydrolysed saccharin solution with ether, and titration of the acid in the extract—the reviser's experiments show that ether is not an efficient solvent. Accurate results are obtained by substituting ethyl acetate for ether and increasing the number of extractions (to 3–6), dissolving in water and re-extracting, but the process is rather tedious.

o-**Sulphonaminobenzoic acid** is a possible though unlikely impurity. It is the only substance which would interfere with the estimation of *o*-benzoicsulphinide and the only way of detecting and estimating it depends on its greater solubility, for which Richmond and Hill publish a table.

o-**Toluenesulphonamide** is detected by the authors as follows. 1 grm. of saccharin and 0.5 grm. of sodium bicarbonate are mixed together and placed in a dry test-tube, about 1 c.c. of water added and the froth kept down by jerking the tube against the hand; when the effervescence slackens a further 1 c.c. of water is added with a continuing of the jerking, and later another 1 c.c., the tube is now closed with the thumb and shaken violently, when the saccharin dissolves completely, leaving the amide undissolved in the form of flocculi. Heavy crystals which settle rapidly are probably undissolved saccharin, indicating that the test has not been carried out properly—the details are important. By extracting the alkaline solution with ethyl acetate and washing with water, the amide can be estimated, but the process is tedious. Good commercial saccharin contains but small traces of this impurity.

Lead and Arsenic.—To estimate lead 2.5 grm. of the sample are boiled with 25 c.c. of water and a few drops of hydrochloric acid, 3 or 4 drops of N/10 sodium thiosulphate solution are added, and the liquid boiled and cooled: 1 c.c. of potassium cyanide solution (free from sulphide) is now added, the liquid made alkaline with ammonia, diluted to 50 c.c., 1 c.c. of a 10% solution of colourless sodium sulphide added and the colour matched with that of a standard solution of lead acetate which has been similarly treated.

The test for arsenic is as follows: 0.25 grm. of saccharin is ignited with 0.25 grm. of magnesium and 0.25 grm. of sodium bicarbonate. After cooling the ash is dissolved in 15 c.c. of 10% sulphuric acid, 5 c.c. of a 10% solution of potassium dithionate added, the sulphur dioxide boiled off, the solution made up to 30 c.c. with 10% sulphuric acid and the arsenic estimated electrolytically, with the use of lead cathodes by Harvey and Hibbert's modification of the Gutzeit test.

The U. S. P. test for *ammonia* by boiling with magnesia is not very delicate, but an estimation may be made if ammonia is present by distilling into standard acid. Ammonia is practically never found except in traces (well below 0.01%).

Easily Carbonisable Organic Matter.—For the British, French and U. S. P. tests by warming with sulphuric acid, Richmond and Hill substitute the test for the para-acid (boiling with 70.5% sulphuric acid) the colour produced being noted.

Sweetness.—By comparing a solution of saccharin containing 0.1 grm. and 0.05 grm. of sodium bicarbonate in 1000 c.c. of water with a 5% solution of cane-sugar, it can be established whether the saccharin is over 500 times as sweet as sugar and by varying the dilution in cases of marked difference, the sweetness of the saccharin can be expressed in terms of cane sugar. With care and experience the authors consider the limit of delicacy of this test to be about 5%.

The application of the physiological so-called "constant" method to the estimation of the sweetening power of sweet substances has been worked out by T. Paul (*Zeitsch. Nahr. Genussm.*, 1922, **43**, 137: abst. *Analyst*, 1922, **47**, 261). It is shown that the sweetening value of saccharin and "dulcin" decreases with the rise in the concentration of the solution.

According to McKie (*J. Soc. Chem. Ind.*, 1921, **40**, 150T) the three useful criteria of purity of saccharin are (*a*) the melting point, (*b*) the solubility in sodium bicarbonate, and (*c*) hydrolysis. Melting-point curves for mixtures of pure saccharin with *o*-sulphamidobenzoic acid and *p*-sulphamidobenzoic acid are given and these show that the melting point is a fairly safe guide as to composition for mixtures containing 0–10% of the para-acid but not in the case of the ortho-compound. As pointed out by Richmond and Hill, the author finds that solution of the saccharin in sodium bicarbonate solution leaves any toluenesulphonamide undissolved. She agrees with Proctor that neither the para-acid nor toluenesulphonamide give ammonia in Reid's method of hydrolysis and concludes that the method, in general, gives fairly accurate results.

Reactions and Detection.—Parmeggiani (*Boll. Chim. Farm.*, 1908, **47**, 37) finds that pure saccharin has the following properties: It is not attacked by nascent hydrogen in alkaline solution, by potassium permanganate, by hydrogen peroxide, or, when cold, by the halogens. Cold nitric acid has no action, but when heated with the acid the sulpho-group is eliminated as sulphuric acid. The most sensitive precipitant for *o*-benzoicsulphinide is mercurous nitrate.

When a solution of saccharin is evaporated with potassium hydroxide and the residue is heated to 250°, salicylic acid is formed, and may be detected by rendering the solution of the residue neutral or faintly acid, and adding ferric chloride, when the characteristic violet coloration will be produced. On igniting a mixture of saccharin and potassium hydroxide or carbonate an odour of benzene is evolved, and on dissolving the residue in water acidified with hydrochloric acid, the solution gives a white precipitate of barium sulphate when barium chloride is added.

Remsen and Burton state that when *o*-benzoic-sulphinide is boiled with dilute acids, it is first converted into 1–2-*sulphaminobenzoic acid*, $COOH.C_6H_4(SO_2NH_2)$, but on continued boiling it is completely changed into *hydrogen ammonium* 1-2-*sulphobenzoate*, $COOH.C_6H_4(SO_3NH_4)$. By evaporating a solution of saccharin with strong hydrochloric acid, *o*-sulphobenzoic acid and ammonium chloride are obtained.

The 1–4-sulphaminobenzoic acid, often present in considerable proportion in commercial saccharin, is unchanged by boiling with dilute acids.

The following are other reactions characteristic of saccharin: If 0.01 grm. to 0.02 grm. is dissolved in 10 c.c. of water containing 2 drops of a 10% sodium hydroxide solution, treated with a solution of *p*-diazonitroaniline, drop by drop, until the greenish-yellow colour of the liquid disappears, and then shaken with 10 c.c. of ether, the ethereal extract, when treated with 20 to 30 drops of the 10% sodium hydroxide solution, gives a fine green ring at the point of contact. On shaking, the ether turns green and the alkali yellowish-brown, whilst the addition of strong ammonia to the ethereal layer decolorises the latter, the ammonia becoming green. With a mixture of saccharin and salicylic acid the reaction gives first a red somewhat brownish ring, then a red aqueous and green ethereal layer. On addition of ammonia the ether is decolorised, whilst the aqueous liquid becomes violet, the shade of colour depending on the proportions of salicylic acid and saccharin present (Riegler, *Pharm. Centr. Halle*, 1900, **41**, 563).

Very dilute solutions of saccharin, when treated with dilute ferric chloride solution followed by hydrogen peroxide, give a violet coloration (Leys, *Compt. rend.*, 1901, **132**, 1056).

If saccharin is heated for 5 minutes at 160° to 170° with a small quantity of a mixture of 5 c.c. of phenol and 3 c.c. of sulphuric acid, and the product dissolved in water, the solution turns purple or rose-red when treated with a little sodium hydroxide solution. (Kastle, *U. S. Pub. Health and Marine Hosp. Serv. Hyg. Lab. Bull.*, 1905, **26**, 31.)

Detection of Saccharin in Foods and Beverages.—Saccharin, being an antizymotic, fulfils 2 requirements in foods and beverages—a preservative and a substitute for sugar.

A large number of methods for the detection of saccharin have been suggested, which differ almost solely in the procedure by which it is isolated. The actual identification is nearly always effected by converting it into salicylic acid which is recognised by the ferric chloride reaction. Necessarily salicylic acid, phenols, tannin, and extractive matter, which react with ferric chloride, must be removed previously. These substances are best eliminated from beverages by the method described by Villiers and his coadjutors (*Rev. Chim. Appl.*, 1904, **7**, 144) and modified by Bianchi and di Nola (*Boll. chim. farm.*, 1908, **47**, 599). The liquid is freed from alcohol by evaporation (repeated if necessary), heated to boiling, acidified with 20 drops of 1% acetic acid per 100 c.c., and treated with excess of lead acetate solution (10 c.c. of 20% solution per 100 c.c.). After standing for 30 minutes the excess of lead is precipitated by addition of a solution containing 10 grm. ot sodium sulphate and the same weight of sodium phosphate per 100 c.c. The liquid is filtered, the filtrate concentrated to 70 or 80 c.c., acidified with 6 or 8 c.c. of 25% sulphuric acid, and extracted 3 times with pure benzene or once with a mixture of equal volumes of ether and benzene. The extract is evaporated almost to dryness and the residual liquid treated with a small quantity of ferric chloride solution (1:1,000) to test for salicylic acid. The benzene is evaporated without removing the ferric chloride, the aqueous residue acidified with 10 c.c. of 10% sulphuric acid, warmed on a water-bath and a solution of potassium permanganate added until a permanent pink colouration is produced. In this way free salicylic acid and substances which simulate or mask the coloration with ferric chloride are destroyed. When cold the liquid is extracted 3 times with pure benzene, the extract evaporated, and the residue dissolved in 2 c.c. of water. If 1 drop of this solution has a sweet taste the remainder is transferred to a test-tube, treated with 2 c.c. of sodium hydroxide solution, evaporated to dryness, and the tube immersed in a fusible-metal bath at 270° for 3 minutes. The fused residue is dissolved in 10% sulphuric acid, the solution extracted with benzene, and the benzene extract filtered and shaken with 5 c.c. of neutral ferric chloride solution (1:1,000). The formation, in the aqueous liquid, of the violet coloration characteristic of salicylic acid, indicates the presence of saccharin in the sample.

Similar methods have been proposed by Boucher and de Bounge (*Bull. Soc. Chim.*, 1903, [iii], **29**, 411), Chace (*J. Amer. Chem. Soc.*, 1904, **26**, 1627), who states that 0.005 grm. of saccharin per litre can be detected by this method, and Jorgensen (*Ann. Falsif.*, 1909, **2**, 58).

Bonamartini (*Rev. intern. Falsif.*, 1906, **19**, 39) has suggested the use of bromine water for the oxidation of tannin and precipitation of salicylic acid, but Boucher and de Bounge state that the permanganate is to be preferred.

Allen concentrates the sample, defecates with lead acetate, acidifies with phosphoric acid, and extracts with ether. The residue from the evaporation of the ethereal solution is fused with sodium hydroxide and the product tested for sulphate. If this is found, saccharin was present. von Mahler (*Chem. Zeit.*, 1905, **29**, 32) fuses the residue with sodium instead of sodium hydroxide and tests the solution of the fused mass for alkali sulphide by means of sodium nitroprusside.

Other solvents have been suggested for the extraction. A mixture of ether and petroleum spirit is recommended by Delle (*Rev. intern. Falsif.*, 1900, **13**, 121), Wirthle (*Chem. Zeit.*, 1900, **24**, 1035), and Spica (*Gazzetta*, 1901, **31**, ii, 41), toluene by Tagliavini (*Boll. chim. farm.*, 1907, **46**, 645) who detects the saccharin in the extract by the formation of a white precipitate with mercurous nitrate solution, and amyl acetate by Parmeggiani (*Boll. chim. farm.*, 1908, **47**, 37).

F. A. Genth, Jr. (*Amer. J. Pharm.*, **81**, 536) extracts saccharin from carbonated beverages with ether, and previous to the extraction of the solution of the alkaline fusion with ether, he exactly neutralises it in the presence of ferric alum solution. The appearance of a violet colour at this stage, renders subsequent operations unnecessary.

Flamand states (*Bull. Soc. chim. belg.* 1913, **26**, 477) that the method of extracting saccharin from beer by means of ether or petroleum spirit, does not give good results when a considerable amount of hops has been used, because the bitter resins extracted simultaneously mask the taste of the saccharin. This difficulty can be met by a preliminary extraction of the beer with benzene, which dissolves the resins, but very little saccharin.

Volhase states (*Chem. Zeit.*, 1913, **37**, 426) that the salicylic acid method is preferable to the recognition of saccharin by conversion of its sulphur into sulphuric acid. Herzfeld and Reischauer (*Naturwiss. Wochschr.*, 1913, 165), however, use a modification of the latter test to detect saccharin in wine and beer. The residue from the ethereal extract is mixed with magnesium powder and heated cautiously to ignition, the product is dissolved in cold water, filtered, and the filtrate tested with sodium nitroprusside solution, a strong violet colour indicating saccharin.

A new test for saccharin has been described by Wauters (7th *Inter. Congr. Appl. Chem.*, London, 1910) and used for the detection of this substance in beer. When saccharin is heated with sulphuric acid and diresorcinol, it yields a product which after treatment with water and filtration gives an intensely violet liquid.

An extraction apparatus for the detection of saccharin in beer has been described by Ledent (*Analyst*, 1913, **18**, 314). It consists of a glass tube 90 cm. long and 1.5 cm. internal diameter fixed vertically and fitted by means of corks, at the top with a stoppered dropping funnel, and at the bottom with a narrow glass tube which is bent round so as to pass up parallel to the wide tube to a height of 35–40 cm. at which point it is bent round and cut off in such a way that the liquid flowing from it can fall into a flask placed below. 50 c.c. of the beer are run into the wide tube and then so much ether that the beer begins to drop from the side tube. The rest of the beer is then run into the wide tube, drop by drop. As the drops fall into the ether they are broken up and the saccharin is extracted, but there is no formation of emulsion, and no preliminary treatment of the beer such as defecation is necessary. If necessary, the beer can be passed through the apparatus several times.

C. von der Heide and W. Lohmann recommend (*Zeit. Nahr. Genussm.*, 1921, **41**, 230–236) the following method for the detection of saccharin in wine: 500 c.c. of the wine are evaporated to about 250 c.c. The liquor thus dealcoholised is cooled, treated with 5–10 c.c. of dilute sulphuric acid (sp. gr. 1.11) and extracted with 100 c.c. of ether in the apparatus described by Ledente. The ethereal solution is washed with water, the greater part of the ether is removed by distillation and the remainder evaporated in a porcelain basin. The dry residue is dissolved in very dilute sodium hydroxide solution, heated on a water-bath and 5% potassium permanganate solution added in small quantities at a time until a persistent red coloration is obtained; sulphuric acid is then added and the mixture again oxidised with permanganate. After the excess of permanganate has been destroyed by the addition of sulphurous acid, the solution is evaporated to about 20 c.c. to expel sulphur dioxide, cooled and extracted three times with ether, using 10 c.c. each time; the ethereal extract is washed with water, evaporated, the residue treated with 3 c.c. of water and again evaporated. This treatment is repeated frequently, so that the heating on the water-bath is prolonged for 1 hour. All benzoic acid is thus removed. If the residue then has a sweet taste, the presence of saccharin is indicated and may be confirmed by fusing the residue with sodium hydroxide and testing for salicylic acid in the usual way. A very similar method has been described by W. Fresenius and L. Grunhut (*Zeit. anal. Chem.*, 1921, **60**, 353–359).

Commanducci publishes (*Boll. chim. farm.*, 1910, **49**, 791) a warning relative to the testing of sweetened foods and beverages for saccharin. He states that when solutions of dextrose and canesugar were extracted with a mixture of equal volumes of ether and petroleum spirit the residue obtained by evaporation of the ethereal extract when heated with sulphuric acid and resorcinol and subsequently treated with alkali and water gave a fluorescent solution the production of which has always been regarded as characteristic of saccharin. If, however, the ethereal extract is washed three or four times with water (which does not remove saccharin) the residue no longer shows this behaviour.

Formenti states (*Boll. chim farm.*, 1902, **41**, 453) that by the following method, 0.001 grm. of saccharin can be detected in 100 c.c. of milk: 100 c.c. of the sample are treated with 1 c.c. of acetic acid (sp. gr. 1.038) and the mixture heated on a water-bath for 30 minutes. The precipitated casein is filtered off and washed, the filtrate and washings acidified with 5 c.c. of sulphuric acid (sp. gr. 1.134) and extracted with 50 c.c. of a mixture of equal volumes of ether and petroleum spirit, a small quantity of alcohol being added towards the end of the extraction. The ether-petroleum extract is evaporated and the residue tested by any of the reactions described above. Salicylic acid, if present, will be extracted with the saccharin.

Spica (*Gazzetta*, 1901, **31**, ii, 41) detects saccharin either by converting the imino nitrogen into nitric acid and identifying this by diphenylamine hydrochloride or by hydrolysis and application of the diazo-reaction.

A method of isolating saccharin from fatty oils is described by Bianchi and di Nola (*Boll. chim. farm.*, 1908, **47**, 183). For its isolation from solid foods, the latter may be extracted with dilute acid, or by gently warming with water, the aqueous or acid extract being treated as already described.

Durand (*J. Ind. Eng. Chem.*, 1913, **5**, 987) recommends the removal of salicylic acid, if present, by means of bromine. An aqueous extract of the sample to be tested is acidified with phosphoric acid and extracted with ether. The ethereal solution is filtered, evaporated to dryness in a nickel basin and a portion of the residue tested for salicylic acid. If the latter is present, the remainder of the residue is dissolved in hydrochloric acid, an excess of bromine added and the mixture filtered; the salicylic acid is thus completely removed as a bromine derivative. The filtrate is then rendered strongly alkaline with sodium hydroxide, evaporated to dryness, and the residue (or the residue from the ethereal solution if salicylic acid is not present) is fused with soda in the ordinary way for conversion into salicylic acid.

Camilla and Pertusi. (*Giorn. Farm. Chim.*, 1911, **60**, 385) isolate saccharin from solid foods by digesting on a water-bath with 2% baryta solution and extracting the filtrate, after acidification with sulphuric or phosphoric acid, with a mixture of ether and benzene. A liquid is concentrated on a water-bath, treated with baryta-water, filtered, and the filtrate after acidifying extracted with the ether-benzene mixture.

Camilla and Pertusi (*Giorn. Farm. Chim.*, 1911, **60**, 385) have described a method of detecting dulcin, salicylic acid and saccharin in the presence of one another.

As the result of the examination of various methods of detecting saccharin in foods M. Klostermann and K. Scholta point out (*Zeit. Nahr. Genussm.*, 1916, **31**, 67–78) that many are vitiated by other substances which may be present, giving the same reactions. They state that the following test is trustworthy. The saccharin is extracted from an acid solution of the foods by means of a mixture of ether and petroleum spirit and the solvent is evaporated. The residue is boiled for 10 minutes with 10% hydrochloric acid and the solution then evaporated to dryness; if this residue has an odour of vanillin, it is extracted several times with a mixture of equal volumes of ether and chloroform, in which mixture saccharin is insoluble. The residue is treated with phenol and phosphoric oxide is added. The development of a red-coloured substance which gives a yellow solution in water, changing to bluish-red on addition of alkali, indicates the presence of saccharin. Ammonium sulphide discharges the bluish-red colour. Besides vanillin, benzaldehyde is the only substance which gives the reaction, and this aldehyde is expelled during the evaporation with hydrochloric acid or is oxidised to benzoic acid, which does not interfere.

Estimation.—The proportion of saccharin present in a sample may often be found by extracting the aqueous solution several times with ether, evaporating the ether, and weighing the residue. Approximation may be often obtained by titrating the aqueous solution with decinormal sodium hydroxide, using litmus or phenolphthalein. 1 c.c. of decinormal alkali neutralises 0.0183 grm. of saccharin.

The following process was devised by Hefelmann (*Pharm. Central. Halle*, 1895, **36**, 228); 10 grm. of the sample are heated with 100 c.c. of 73% sulphuric acid for 5 hours, the vessel being immersed in boiling water and frequently shaken. The mixture is then cautiously diluted with 100 c.c. of water, cooled, a crystal of pure 1–4-sulphamidobenzoic acid added, and the solution allowed to stand for at least 12 hours. When only small amounts of the 1–4 compound are present, it may be necessary to allow the solution to stand for several days. The 1–4 acid separates almost entirely. It is collected in a Gooch crucible provided with a double strainer and an asbestos filter, washed with water until the acid reaction is removed, dried at 100° to constant weight and weighed. The loss due to the slight solubility of the precipitate in cold water is not serious. The material should melt at from 270° to 280°.

The filtrate and washings are made up to 500 c.c. with water, 50 c.c. of this mixed with excess of magnesium oxide, and distilled. Ammonium hydroxide is formed, which is absorbed by dilute standard acid as in the Kjeldahl method. From the amount of ammonium nitrogen thus indicated the saccharin in the original material can be calculated: 1 part of nitrogen is equivalent to 13.07 parts of saccharin.

The principle of the above process is due to Remsen and Burton (*Amer. Chem. J.*, 1889, **11**, 403) who used dilute hydrochloric acid instead of the relatively strong sulphuric acid employed by Hefelmann. Reid (*Amer. Chem. J.*, 1899, **21**, 461) found that the hydrolysis is best effected by dilute hydrochloric acid, and that the ammonia can then be distilled off, after making the liquid alkaline, as in the ordinary Kjeldahl process. Reid's method is as follows: 0.5 to 1 grm. of the sample is weighed into a 100 c.c. flask and 50 c.c. of approximately normal hydrochloric acid added. The flask is fitted with an air-condenser (45 cm. long by 8 mm. diameter) and heated on a sand-bath for 2.5 hours, so that the liquid is kept gently boiling. The condenser is then removed and the liquid concentrated to about 10 c.c. and washed into a distillation-flask. 20 c.c. of a 50% solution of sodium hydroxide are added and the ammonia distilled into a known volume of standard acid, the excess being titrated with standard potassium hydroxide, with the use of cochineal as indicator.

The ammonia is formed from the *o*-benzoicsulphinide (and any ammonium salts present as impurities), the *p*-sulphaminobenzoic acid not being attacked in the process. Since *o*-benzoicsulphinide is not attacked by alkali hydroxide solutions, the amount of ammonium salts present, if any, can be estimated by distilling a separate portion of the sample with sodium hydroxide solution.

Proctor has employed Reid's process and gives results showing that it is quite reliable even in the presence of considerable amounts of the para-compound or of such possible impurities as toluene-*o*-sulphonamide (*Trans.*, 1905, **87**, 242).

Proctor finds that iodine is liberated from a solution of potassium iodide and iodate by saccharin and, more slowly, by *p*-sulphaminobenzoic acid, the reaction being quantitative. The powder (0.5–1.0 grm.) is weighed into a 150 to 200 c.c. flask with a well-fitting stopper, and 50 to 75 c.c. of water added. A crystal or two of potassium iodide is dropped into the mixture, 10 c.c. of a 5% potassium iodate solution added and the mixture shaken gently. Pure *o*-benzoic-sulphinide dissolves almost immediately, liberating an equivalent weight of iodine, which is titrated against standard sodium thiosulphate solution. The presence of any large proportion of *p*-sulphamino-benzoic acid causes the powder to dissolve much more slowly and frequent shaking during 15 to 20 minutes may be required to effect the complete solution necessary before titration. If the proportion of the para-compound present is small, the number of c.c. of N/10 thiosulphate solution used, multiplied by 0.0183 gives very approximately the total weight of *o*-benzoicsulphinide and *p*-sulphamino-benzoic acid present.

A rapid, though only approximate, method of estimating the proportions of real saccharin and the para-compound in a sample, is based on the titration of 3 to 5 grm. of the latter with standard alkali, using phenolphthalein as indicator. 1 grm. of saccharin neutralises 54.6 c.c., whilst the same weight of *p*-sulphaminobenzoic acid requires 49.7 c.c. of N/10 sodium hydroxide solution. From the volume of alkali required the percentage of each substance is easily calculated (*Pharm. Post.*, 1901, **31**, 234).

For the examination of saccharin tablets H. D. Richmond, S. Royce and C. A. Hill recommend (*Analyst*, 1918, **43**, 402–404) a modification of the above method (see p. 414) since the presence of theobroma emulsion or a similar substance containing soap causes excessive frothing when the tablets are boiled with alkali solution. The alkalinity of the tablets is determined by boiling one with excess of N/10 sulphuric acid and titrating the excess of acid with N/10 sodium hydroxide solution, using phenolphthalein as indicator. Twenty tablets are then weighed, treated with 25 + x c.c. of 4 N sulphuric acid (where x c.c. of N/10 sulphuric acid represents the alkalinity of a single tablet), the mixture diluted to 50 c.c. and boiled under a reflux condenser for 1.5 hours. To the resulting solution 20 c.c. of 7.5 N sodium hydroxide solution are added together with a little powdered pumice, the ammonia distilled into 20 c.c. of N/5 acid and the excess of acid titrated, with the use of methyl-red as indicator.

In the examination of saccharin tablets A. Bonis (*Ann. Falsif.*, 1918, **11**, 369–372) estimates free sodium bicarbonate by titrating with N/10 sulphuric acid and methyl orange, free saccharin by extracting with ether and total saccharin by fusing the sample with sodium carbonate and sodium nitrate and precipitating the sulphate formed as barium sulphate.

O. Beyer, after an investigation of various methods which have been proposed for the estimation of saccharin (*Chem. Zeit.*, 1919, **43**, 537–538), rejects those of Reid, Fahlberg, Klages, Hefelmann and Proctor (iodometric), and concludes that only two are trustworthy, namely that depending on the hydrolysis of the substance with 20% sulphuric acid and that of Richmond and Hill.

According to C. B. Gnadinger (*J. Assoc. Off. Agric. Chem.*, 1917, **3**, 25–32) saccharin is more readily extracted from a solution acidified with hydrochloric acid than from one acidified with acetic acid. The best solvents are ethyl acetate and ether; chloroform is unsuitable. In the provisional method of the Association of Official Agricultural Chemists, the amount of saccharin is calculated from the weight of sulphur estimated in the ethereal extract, but this method is not applicable to foods containing ground mustard since sulphur compounds in the mustard are simultaneously extracted. These may be eliminated, however, by evaporating the extract and treating the residue with petroleum spirit and then with bromine: From 50 to 75 grm. of the material are digested with about 200 c.c. of nearly boiling water for 2 hours with occasional shaking, then treated with 5 c.c. of glacial acetic acid and a slight excess of 20% normal lead acetate solution, made up to 250 c.c. with cold water, left for 20 minutes, centrifuged and filtered. 150 c.c. of the filtrate are acidified with 15 c.c. of hydrochloric acid and extracted for 2 minutes each time with three successive portions of 80 c.c. of ether. The united extracts are washed with 5 c.c. of water and mixed with 10 c.c. of sand, and the ether is evaporated with the aid of a bellows. When the residue is quite dry it is thoroughly mixed with 25 c.c. of petroleum spirit (b. p. 30° to 65°), the extract decanted on to a filter and the extraction repeated with two fresh portions of solvent. The residual sand is then washed with hot water and the washings filtered into a separating funnel. The filtrate (about 75 c.c.) is cooled, mixed with 7–8 c.c. of hydrochloric acid and treated with excess of bromine-water. After 5 minutes the excess of bromine is removed by means of a slight excess of sodium nitrite solution and the acid solution is extracted with three successive portions (50 c.c. each) of ether. The ethereal extract is washed with 5 c.c. of water, and the ether allowed to evaporate spontaneously. The sulphur in the residue is estimated by fusion in a nickel crucible with sodium peroxide or with a mixture of sodium carbonate and potassium nitrate (6 : 1). The weight of barium sulphate obtained multiplied by 0.7844 gives the weight of saccharin, and to this should be added 0.0005 grm. as a correction for the saccharin dissolved by the petroleum spirit. To prevent loss of sulphur through imperfect oxidation during the fusion, an electrolytic method may be used. The residue from the ethereal extract is dissolved in hot water and filtered and the filtrate and washings (about 75 c.c.) are mixed with 25 c.c. of 16% sodium hydroxide solution and electrolysed for 6 hours, with smooth platinum electrodes (area of anode about 120 sq. cm. and of cathode about 1 sq. cm.) by means of a current of 2.7–2.9 amps. The electrolysed solution is rendered slightly acid with hydrochloric acid and the sulphuric acid is precipitated with barium chloride. A blank estimation should be made of the amount of sulphur in the 25 c.c. of sodium hydroxide solution.

Parmeggiani (*Boll. chim. farm.*, 1908, **47**, 37) states that saccharin in foods can be very accurately estimated by the following process: The liquid (or aqueous extract of a solid food) is concentrated, treated as described under *Detection* in order to remove salicylic acid and extractive matter, and extracted several times with a mixture of equal volumes of ether and petroleum spirit. The combined extracts are washed with water, evaporated to dryness, and the residue titrated with N/200 sodium hydroxide solution. For the estimation of saccharin in foods containing benzoic acid, Testoni (*Zeit. Nahr. Genussm.* 1909, **18**, 577) recommends that the ether extract of the food should be heated at 110° to 115° to volatilise the benzoic acid. Another method is to precipitate the saccharin from an alcoholic solution of the extract, as silver saccharinate, $AgC_7H_4SO_3N$, by addition of silver nitrate solution. After standing 12 hours the precipitate is collected on a Gooch crucible, washed with alcohol, dried at 100° and weighed. A method of estimating saccharin in cocoa powder, depending on the fusion of the substance, when isolated, with sodium carbonate and nitrate and estimation of the sulphate formed, is described by van den Driessen Mareeuw (*Pharm. Weekblad*, 1907, **44**, 245).

To estimate saccharin in foods rich in fat, starch and proteins, Tortelli and Piazza (*Zeitsch. Nahr. Genussm*, 1910, **20**, 489) recommend the following process. A weighed quantity of the sample is mixed with about 18 grm. of fine sand and 10 grm. of slaked lime (liquids are evaporated to the consistence of a paste after the addition of the sand and lime) and the mixture is extracted four times with quantities of 50 c.c. of boiling 95% alcohol, 10 c.c. of a saturated solution of sodium chloride being added each time. The alcoholic solution is filtered, the filter washed with a mixture of alcohol and sodium chloride solution, and the filtrate evaporated to about 80 c.c. When cold, the residual liquid is mixed with 10 c.c. of saturated sodium chloride solution, and extracted several times with petroleum spirit. After the fatty substances have been thus removed, the liquid is heated on a water-bath until all traces of alcohol have been expelled; it is then cooled, acidified with sulphuric acid, and extracted several times with a mixture of equal volumes of ether and petroleum spirit. The ethereal extracts are washed once with water, filtered and evaporated and the residue weighed. If the substance known as "dulcin" or "sucrol" (*p*-phenetolecarbamide) is present, it may be separated by extracting with ether before acidification. Dulcin melts at 173°, saccharin at 223°. When a trace of the former substance is suspended in water and heated with mercuric nitrate solution (free from nitric acid) a violet coloration develops within 15 minutes, and may be made more intense by addition of a small quantity of lead peroxide.

A. Baumann finds (*Zeit. ges. Brauw.*, 1920, **43**, 137–139) that Tortelli and Piazza's method gives satisfactory results, but the saccharin isolated is liable to be contaminated with impurities which prevent its crystallisation. This difficulty the author avoids in the following way. The residue of saccharin (from 1000 c.c. of beer) left on distilling the ether and petroleum spirit solution is dissolved in alcohol and treated with a few drops of potassium hydroxide solution and then with a few c.c. of sodium chloride solution and two or three times this quantity of water, shaken with petroleum spirit and the solution distilled until free from alcohol. The residual liquid is cooled, acidified with 3–4 c.c. of 10% sulphuric acid and again extracted three or four times with the mixture of ether and petroleum spirit. This extract is washed with a little water to remove acid, and filtered. On evaporating the filtrate *in vacuo* the saccharin is obtained crystalline and almost white.

Possetto and Issoglio (*Giorn. Farm. Chim.*, 1912, **61**, 5) separate the saccharin by dialysis. In the case of milk and milk preparations 50 c.c., of jams and fruit jellies 50 grm., and of candied fruits, sweets, or cocoa 30 grm., are made alkaline with sodium carbonate solution and dialysed for 12–24 hours. The yellow solution produced is acidified with phosphoric acid and extracted twice with ether. The ethereal solution is washed, filtered, evaporated and the residue tested for salicylic acid. If this be present, it may be separated either by treating the original solution after dialysis with bromine water and filtering, or with permanganate and sulphuric acid and filtering after 12 hours standing, the saccharin being afterwards extracted with ether (after acidifying with phosphoric acid if bromine be employed).

Other methods are described by Condelli (*Staz. sperim. agrar. ital.*, 1914, **47**, 308) and Karas (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 559). A method of estimating saccharin and saponin in oil emulsions is published (*Boll. chim. farm.*, 1911, **50**, 609) by Carlinfanti and Marzocchi, and a colorimetric method of estimating saccharin in urine has been described by Bloor (*J. Biol. Chem.*, 1910, **8**, 227).

Ceccherelli states (*Ann. Falsif.*, 1915, **8**, 109) that in estimating saccharin treatment of the ether extract with potassium permanganate is not to be recommended, although it is useful in making qualitative tests. Gum tragacanth, extract of gentian and certain other substances after fusion with sodium hydroxide produce colorations with ferric chloride and may therefore interfere with this method of testing for saccharin. Tarugi and Lenci (*Rend. Soc. Chim. Ital.*, 1911, **7**, 320) have described the following test, based on the liberation of the amino-group. A minute quantity of saccharin, heated with a few drops of sulphuric acid until white fumes appear, then cooled, diluted with water, neutralised with soda and added to a solution of a crystal of phenol in sodium hydroxide solution, gives a blue colour on addition, drop by drop, of a fresh solution of sodium hypochlorite.

The author concludes that there is at present no satisfactory means of estimating saccharin, applicable to all cases, but the presence of this substance may be regarded as certain if the ether extract, after treatment with permanganate, yields a residue which glistens slightly, contains sulphur, yields an insoluble silver salt containing 37% of silver, gives the reactions of salicylic acid after fusion with soda but not before, and also responds to the above test after hydrolysis.

Ceccherelli further states (*Boll. chim. farm.*, 1915, **54**, 641–648) that, before a foodstuff is treated with ether in order to extract any saccharin present, it is necessary to expel any alcohol completely, since even a small residuum of this solvent may result in the extraction of other sweet substances such as glycerol, lævulose, various glucosides, etc. In some cases the whole of the alcohol is not expelled by a single evaporation, and it is advisable to evaporate repeatedly after taking the residue up with distilled water.

G. S. Jamieson has described (*J. Biol. Chem.*, 1920, **41**, 3–8) a method of estimating saccharin in urine. The urine is treated with lead acetate and filtered. After acidifying the filtrate with hydrochloric acid, the saccharin is extracted with ether, the ether removed by evaporation and the saccharin in the residue again extracted with ether. The second ethereal solution is evaporated, the residue fused with sodium carbonate and sodium nitrate, and the amount of saccharin deduced by estimation of the sulphate.

CINNAMIC ACID AND ITS DERIVATIVES

Cinnamic Acid. β-Phenyl-acrylic Acid

$$C_9H_8O_2 = C_8H_7CO.OH = C_6H_5.CH{:}CH.COOH$$

Cinnamic acid occurs free and as esters in liquid storax, Tolu and Peruvian balsams, in Sumatra benzoin, and in old oils of cinnamon and cassia, which sometimes deposit it in large crystals.

For the methods of synthesis see Miller (*Annalen*, 1877, **188**, 196) and Perkin (*Trans.*, 1877, **31**, 389). It is manufactured by the action of sodium acetate on benzylidene chloride.

Cinnamic acid crystallises in colourless, monoclinic prisms or laminæ having a sp. gr. of 1.247. It melts at 133° and distils, with more or less decomposition, at about 300°.

J. Kachler (*Ber.*, 1869, **2**, 512) gives the following table showing the m.p. of various mixtures of cinnamic and benzoic acids:

Cinnamic acid, %	Benzoic acid, %	M. p., °
100	0	133.3
99	1	131.8
90	10	126.6
80	20	118.0
70	30	108.2
60	40	98.7
50	50	84.3
40	60	87.1
30	70	101.4
20	80	106.4
10	90	111.5
1	99	118.2
0	100	123.3

Cinnamic acid dissolves sparingly in cold water (1 in 3,500 at 17°), but readily in boiling water, alcohol, and ether.

According to T. Bokorny, whilst cinnamic acid (in the form of 0.1% solution) is a good bactericide, the sodium salt is much less active, a 1% solution being required to show any antiseptic action. The germicidal properties of cinnamic acid are stated to be greatly enhanced if used in conjunction with a little tartaric acid.

H. Serger agrees (*Chem. Zeit.*, 1914, **38**, 354–356) that cinnamic acid has a greater preservative action than its sodium salt, and states, further, that it is superior to benzoic acid in this respect.

Reactions.—Cinnamic acid, when slowly heated alone, or more readily if heated with lime, splits into carbon dioxide and cinnamene, C_8H_8, a small quantity of stilbene, $C_{14}H_{12}$, being also produced.

A neutral solution of a cinnamate gives a precipitate with manganous salts, at first white but afterwards becoming yellow and crystalline (benzoates give no precipitate). The precipitate formed with ferric salts is yellow.

Cinnamic acid is also distinguished from benzoic acid by the smell of bitter-almond oil developed on warming it with chromic acid mixture. The same odour is produced by boiling cinnamic acid with water and lead dioxide, the latter substance gradually becoming yellow, and being partially converted into lead benzoate.

When fused at a moderate temperature with potassium hydroxide cinnamic acid is split up, with evolution of hydrogen and formation of potassium acetate and benzoate—$C_9H_8O_2 + 2KHO = KC_2H_3O_2 + KC_7H_5O_2 + H_2$. The presence of an acetate in the product is a proof of the existence of cinnamic acid in the original substance.

Benzoic acid may be separated from cinnamic acid by crystallisation from boiling alcohol. The acids may also be separated by distillation in a current of steam, when benzoic acid nearly free from cinnamic acid passes over. By careful sublimation the benzoic acid may also be completely separated, as little cinnamic acid volatilises below 200°.

Cinnamic acid may be detected in presence of benzoic acid by Jorissen's reaction (compare p. 372).

For the detection of benzoic acid in cinnamic acid Lunge (*Chemisch-technische Untersuchungsmethoden*, 1905, **3**, 860) gives the following method: 1 grm. of the sample is shaken for an hour with 100 c.c. of water at 20° and the liquid filtered. 50 c.c. of the filtrate are titrated with N/10 sodium hydroxide solution using phenolphthalein as indicator. If the sample is pure, the volume of alkali used will be 1.4 c.c., whilst in the presence of benzoic acid, which is more than 5 times as soluble as cinnamic acid, a larger volume will be required. Pure benzoic acid by this process gives a filtrate 50 c.c. of which neutralise 11.2 c.c. of N/10 alkali. By this test 1% of benzoic acid can be detected.

Detection.—For the detection of cinnamic acid in urine von der Heide and Jakob (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 137) proceed as follows. A portion of the urine is rendered alkaline, evaporated to a small volume, acidified and extracted with ether. The ethereal solution is shaken with dilute alkali solution. The aqueous alkaline solution is heated on a water-bath until all the dissolved ether has been expelled, cooled and treated with 1% potassium permanganate solution; the first few drops of the latter convert any cinnamic acid present into benzaldehyde which may be recognised by its odour. As little as 0.00001 grm. of the acid gives a distinct smell of benzaldehyde.

A similar method is recommended by Schenk and Burmeister (*Pharm. Zeit.*, 1915, **60**, 213). The substance in which cinnamic acid is to be detected is acidified with phosphoric acid and extracted with ether; the ethereal solution is then shaken with sodium carbonate solution, the aqueous layer separated, extracted twice with ether (this is essential, particularly in the case of fruit juices, in order to remove small quantities of furfuraldehyde compounds), and very dilute potassium permanganate solution is added, drop by drop, until the pink colour is only just discharged. The solution is now extracted with ether, the ethereal solution treated with 10 drops of a 5% ethereal solution of phenol and allowed to evaporate at the ordinary temperature. On adding a few drops of concentrated sulphuric acid to the residue a yellow coloration is obtained, even when the quantity of benzaldehyde formed from the cinnamic acid is too small to be identified by its odour. The furfuraldehyde compounds which may be present give, if not removed completely, a faint orange coloration which cannot be mistaken for that yielded by benzaldehyde.

Tunmann has devised (*Pharm. Zentr. h.*, 1913, **54**, 133) a microsublimation method of detecting cinnamic acid, especially in resins.

Bigelow recommends the following process for detecting cinnamic acid in foods (*U. S. Dept. Agric. Bull. No.* 122, 1909, 77). A mixture of 100 grm. of the food with 100 c.c. of water and 5 c.c. of sulphuric acid (1:5) is extracted three times with (50 c.c., 25 c.c., and 25 c.c.) chloroform, and the combined extracts evaporated to dryness after being rendered alkaline with ammonia. The residue is heated to boiling with 5 c.c. of dilute chromic acid mixture (1 part of dilute sulphuric acid saturated with potassium dichromate, and 7 parts of water). The odour of benzaldehyde is most apparent after cooling the liquid so that sulphuric acid fumes are no longer evolved. The method will detect 0.025 grm. of cinnamic acid per kilogram.

G. Denigès has described (*Bull. Soc. Chim. pharm. Bordeaux*, 1919, **57**, 209–212) a method of detecting cinnamic acid by oxidising it to benzaldehyde by means of ferric chloride and hydrogen peroxide solutions.

Estimation.—Lunge (*loc. cit.*) estimates the cinnamic acid in a sample by dissolving 1 grm. in 10 c.c. of N-alkali and titrating back with N-acid. 1 c.c. of N-sodium hydroxide solution corresponds to 0.148064 grm. of cinnamic acid.

Cinnamic acid combines with 2 atoms of bromine when treated with excess of this reagent under suitable conditions. In this way cinnamic acid may be estimated in admixture with benzoic acid, which does not take up bromine directly. The following directions are given by De Jong (*Rec. trav. chim.*, 1909, **28**, 342). About 2 grm. of mixed acids are dissolved in carbon disulphide, the solution treated with bromine and allowed to stand for 24 hours. The solvent and excess of bromine are then distilled, and the residue dissolved in ether. The ethereal solution is evaporated to dryness at ordinary temperature, and the residue dried over sulphuric acid *in vacuo*. The solid is then powdered and heated at 100° in Ruber's apparatus (*Anal. u. Konst. org. Verb. von. H. Meyer*, 1903, p. 14) and the residual phenyldibromopropionic acid weighed. It is claimed that the separation is quantitative.

The method of De Jong has been modified by him (*Rec. trav. chim.*, 1911, **30**, 223) in order to facilitate the combination of cinnamic acid with bromine. The acid is dissolved in sodium hydroxide solution and reprecipitated with hydrochloric acid. The resulting magma is treated with N/50 aqueous solution of bromine until the yellow coloration produced persists for 5 minutes. Then excess of potassium iodide solution is added and the free iodine titrated.

Bougault and Mouchel-la-Fosse (*Compt. rend.*, 1913, **156**, 396) for the estimation of cinnamic in the presence of benzoic acid make use of the action between the former acid and sodium hydrogen sulphite. The acid is allowed to combine with a known volume of a standardised solution of the sulphite, the excess of which is then titrated with standard iodine solution.

The estimation may also be made as described under Salicylic Acid (p. 497).

CINNAMIC ESTERS

Methyl cinnamate, $CH_3.C_9H_7O_2$, forms crystals melting at 33° and boiling at 263°. It is an important constituent of the essential oil of the rhizomes of *Alpinia Malaccensis*, and is also present in the leaves of the same plant. Other oils derived from plants of the same species probably contain this ester.

Ethyl cinnamate, $C_2H_5.C_9H_7O_2$, is produced by distilling together cinnamic acid, alcohol, and strong sulphuric acid; or by saturating a strong solution of cinnamic acid in alcohol with hydrogen chloride. It is a limpid liquid having sp. gr. 1.3 and b. p. 271°.

Benzyl Cinnamate. Cinnamein. $C_7H_7.C_9H_7O_2$. This substance exists ready-formed in Peru and Tolu balsams. It may be obtained with some admixture of cinnyl cinnamate by treating the former substance with carbon disulphide, separating the insoluble matter, and distilling off the solvent from the solution.

Benzyl cinnamate has an agreeable taste and feeble aromatic odour, resembling that of Peruvian balsam, but without the empyreumatic smell observable in the latter. It is commonly described as an oily liquid which is liable to solidify with conversion into a crystalline isomeric substance called metacinnamein. But when obtained pure by boiling together benzyl chloride, alcohol, and dry sodium cinnamate, it forms short shining white prisms, m. p. 39°, which may remain liquid for a considerable time if cooled to 0°. Benzyl cinnamate has sp. gr. 1.098 in the liquid state, and b. p. 225° to 235° with slight decomposition. It is nearly insoluble in water, but is readily dissolved by alcohol, ether, carbon disulphide, etc.

By long exposure to air and light, benzyl cinnamate acquires an acid reaction. It is readily saponified by alcoholic potassium hydroxide with formation of potassium cinnamate and benzyl alcohol, $C_7H_7.OH$.

Phenyl cinnamate, $C_6H_5C_9H_7O_2$ has m. p. 72.5° and b. p. 206° 15 mm.; at ordinary pressure it boils with decomposition. *Phenyl propyl cinnamate* occurs in small amount in Sumatra benzoin, in storax, and yellow resin.

Cinnamyl Cinnamate. Styracin. $C_9H_9.C_9H_7O_2$. This substance occurs together with benzyl cinnamate in liquid storax, and Peru and Tolu balsams. It crystallises in tufts of beautiful prisms, m. p. 44°, which are devoid of smell or taste. It distils without decomposition in steam heated to 180°. Cinnamyl cinnamate is insoluble in water and but sparingly soluble in cold alcohol or petroleum spirit, but is easily soluble in ether or carbon disulphide. When treated with alcoholic potassium hydroxide it is saponified with formation of potassium cinnamate and

Cinnamyl Alcohol, Styryl Alcohol, Styrone, β-Phenylallylalcohol, $CHPh:CH.CH_2.OH$. When cinnamyl cinnamate is cautiously distilled with aqueous potassium hydroxide, a milky distillate is obtained, and on saturating it with common salt the cinnamyl alcohol forms a creamy or oily layer on the surface. It may also be extracted from the distillate or the original liquid by agitation with ether.

Cinnamyl alcohol forms soft, silky needles, m. p. 33°, b. p. 250°, having a sweet taste and an odour of hyacinths. It is soluble in about 12 parts of cold water, a hot saturated solution becoming milky on cooling and remaining so for several hours, when the cinnamyl alcohol separates in crystalline needles, very soluble in alcohol and ether.

Cinnamyl alcohol possesses valuable antiseptic properties, being as powerful in this respect as thymol.

Cinnamyl alcohol is converted by cautious oxidation into cinnamic aldehyde and cinnamic acid. With chromic acid mixture it becomes hot and yields cinnamic acid, which separates on the surface, and on heating this becomes further oxidised to benzaldehyde.

Cinnamene, styrene, or phenyl-ethylene $(C_6H_5)CH:CH_2$, exists in small quantity ready-formed in liquid storax (page 468), and may be extracted by distilling the balsam with water to which sodium carbonate has been added to neutralise the free cinnamic acid. The hydrocarbon passes over with steam, and collects as an oil on the surface of the distillate. Cinnamene may also be obtained synthetically, and, as stated above, by heating cinnamic acid alone or in admixture with lime or baryta. The reaction in the latter case is exactly parallel to that by which benzene is produced from benzoic acid and methane from acetic acid.

Cinnamene is a colourless, mobile liquid, of sp. gr. 0.925 at 0°, having a pleasant aromatic odour. It remains fluid at $-10°$ and boils at 144°, the temperature of the contents of the retort being liable to rise suddenly from formation of metacinnamene.

Stilbene, or diphenyl-ethylene, $(C_6H_5)CH.CH(C_6H_5)$, crystallises in nacreous plates, m. p. 124°, b. p. about 306°. It unites with bromine to form a dibromide, $C_{14}H_{12}Br_2$, of which 2 stereoisomeric modifications exist, the α, m. p. 237°, and the β, m. p. 110 to 110.5°.

CINNAMIC ALDEHYDE. CHPh : CH.CHO

This occurs in oils of cassia and cinnamon, of which it constitutes the greater part.

Hanuš (*Zeit. Nahr. Genussm.*, 1904, 7, 669) found the following amounts of cinnamaldehyde in the different varieties of cinnamon:

Ceylon cinnamon, 1.74 to 2.19%; cassia cinnamon, 2.08 to 3.81%; buds of the latter, 3.70 to 6.00%; cinnamon chips 1.23 to 1.42%.

For the synthesis of cinnamaldehyde see Peine (*Ber.*, 1884, **17**, 2117).

Cinnamaldehyde is a colourless oil, rather denser than water. It may be distilled in a vacuum, or with water free from air. On exposure to the air, it quickly becomes yellow and resinous, and acquires an acid reaction. It rapidly absorbs oxygen, especially in presence of moisture, and is converted into cinnamic acid. Chromic acid converts it into benzoic and acetic acids.

Estimation.—Schimmel & Co. estimate cinnamaldehyde in cinnamon and cassia oils by the following process:

A special flask with a somewhat flat-bottomed bulb and long neck is used. The bulb holds about 100 c.c. The neck is about 13 cm. long, has a calibre of 8 mm., and is graduated to read to 0.1 c.c. The total capacity of the neck is a little over 6 c.c. The zero-mark is slightly above the point at which the neck joins the bulb. 10 c.c. of oil are transferred to the flask and 10 c.c. of a 30% solution of sodium hydrogen sulphite added. The mixture is shaken and immersed in boiling water. When the mass has melted, more sodium hydrogen sulphite solution is added and, still shaking, the addition of small amounts of sulphite is continued until the volume of the mixture is about 75 c.c. The heating is continued until no more solid particles are present and the odour of cinnamaldehyde has disappeared. When the clear oil floats upon the salt solution, the flask is removed from the bath, and when the contents are cold, sufficient sulphite solution is added to raise the lower limit of the oily layer to zero. The amount of oil is then read off, and by deducting this number from 10, the volume of cinnamaldehyde in the sample is obtained. As the sp. gr. of the aldehyde and other constituents are nearly the same, the reading may be taken as percentage by weight.

Burgess (*Analyst*, 1904, **29**, 78) advocates a similar method, but uses neutral sodium sulphite and neutralises the alkali as it is formed in the action by the gradual addition of acetic acid, phenolphthalein being present as indicator. The action is complete when the liquid ceases to become alkaline on standing after further addition of sulphite.

The process employed by Pouchand (*Schweiz. Woch. Chem. Pharm.*, 1904, **42**, 146) is based on the same principle.

C. T. Bennett and F. C. L. Bateman state (*Perf. Ess. Oil Rec.*, 1923, **14**, 268–270) that in the bisulphite method 5 c.c. of oil give better results than do 10 c.c., and that the best results are obtained if not less than 50 c.c. of sodium bisulphite solution are used. The authors point out that sodium bisulphite powder deterioriates, and its use may lead to low results; the crystals are more stable but take longer to dissolve. Potassium metabisulphite is more stable than the sodium salt, and is also a better absorbent for aldehydes, this being probably due to the potassium sulphonate compounds being more soluble and more readily formed than the sodium salts.

The U. S. Pharmacopœia gives the following method of analysis.

> Introduce 10 c.c. of the oil into a 200 c.c. flask with a long graduated neck (cassia flask) by means of a pipette, add 50 c c of a saturated solution of sodium sulphite which has been carefully rendered neutral to phenolphthalein by means of acetic acid, heat the mixture in a bath containing boiling water and shake the flask repeatedly, neutralising the mixture from time to time by the addition of a few drops of acetic acid. When no coloration appears upon the addition of a few more drops of phenolphthalein and heating for 15 minutes, cool and when the liquids have separated completely, add sufficient of the sodium sulphite solution to raise the lower limit of the oily layer within the graduated portion of the neck and note the volume of the residual liquid.
>
> The oil should show not less than 80% by volume of cinnamaldehyde.

S. S. Sadtler follows Burgess's directions, but estimates the aldehyde by determination of the amount of alkali formed in the reaction. 12 drops of the oil are weighed into a 150 to 200 c.c. flask, mixed with 5 c.c. of water and a few drops of rosolic acid solution, and the liquid exactly neutralised with N/10 alkali. 50 c.c. of a 20% sodium sulphite solution are added and the flask immersed in boiling water. Sufficient N/2 hydrochloric acid is gradually added to keep the liquid neutral, whilst the flask is continuously heated and shaken. When a condition of permanent neutrality is reached, the volume of N/2 acid used, is noted. A blank experiment is made, exactly the same quantities of reagents but no aldehyde being used. The volume of N/2 hydrochloric acid required is deducted from that used in the estimation. Each c.c. of difference corresponds to 0.033 grm. of cinnamaldehyde.

J. Hanuš (*Zeit. Nahr. Genussm.*, 1903, **6**, 817) found that cinnamaldehyde, both pure and as it occurs in cinnamon and cassia oils, may be quantitatively precipitated in the form of semioxamazone,

$$C_6H_5.CH:CH.CH:N.NH.CO.CO.NH_2,$$

by treating an aqueous suspension with a solution of semioxamazide in hot water. 0.10 grm. of the aldehyde is weighed off, emulsified by agitation with 100 c.c. of water treated with 0.25 to 0.35 grm. of semioxamazide in 15 c.c. of hot water; the mixture is well shaken together, occasionally for 3 hours, then allowed to stand for 24 hours. The crystalline cinnamaldehyde semioxamazone is then collected on a tared Gooch filter, washed with cold water, dried at 105° for about 4 or 5 hours, then weighed. The weight of semioxamazone, multiplied by the factor 0.6083, gives the amount of cinnamaldehyde present. For the estimation of the amount of aldehyde in cinnamon and cassia oils from 0.15 to 0.2 grm. should be employed.

To estimate the amount of cinnamaldehyde in cinnamon or cassia barks, from 5 to 8 grm. of the finely ground material are distilled with steam until about 400 c.c. of distillate have been collected. The volatile oil is extracted from the distillate by shaking out 3 or 4 times with ether, and after distilling off the ether, the oil is emulsified and treated with semioxamazide as described above. By this method commercial cinnamaldehyde has been found to yield from 99.21 to 100. 66%, commercial cinnamon oil from 46.78 to 80.51% of cinnamaldehyde; Ceylon cinnamon oil from another source, 79.05 to 80.33%. Synthetic cassia oil, 95.19 to 95.58% of cinnamaldehyde. Cinnamon bark was found to yield from 1.75 to 2.04% of aldehyde.

It is claimed that the method gives results more accurate than those of the sulphite absorption process generally employed. With commercial cinnamaldehyde, Allen obtained figures which were nearly 5% lower than those given by the sulphite method. With the natural oils, however, the latter method gave results from 4 to 6% lower than this gravimetric process.

Th. von Fellenberg has devised (*Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 254–266) a colorimetric method of estimating cinnamaldehyde. 1 grm. of the cinnamon is placed in a flask, together with 40 c.c. of 95% alcohol, and the mixture is heated just to boiling for 10 minutes, the flask being attached to a condenser and any distillate collected in a 100 c.c. flask. From 30–35 c.c. of alcohol are then distilled, 100 c.c. of boiled water are added to the flask and the distillation is continued until the total distillate measures 100 c.c. 5 c.c. of the distillate are then mixed with 2 c.c. of a 5% solution of isobutyl alcohol in 95% ethyl alcohol and 3 c.c. of 38% alcohol; 20 c.c. of concentrated sulphuric acid are added and, after 45 minutes, the colour developed is compared with that given by a known amount of cinnamaldehyde under similar conditions. The standard solution used for comparison contains 2% of cinnamaldehyde in 38% alcohol; it may be prepared from the aldehyde-sulphite compound and standardised by a bromine-iodine titration.

Oil of Cinnamon. Oil of Cassia.—The volatile oil of cinnamon is prepared by distilling the chips and refuse bark with water.

The oil of Ceylon cinnamon is a pale yellow or reddish liquid, becoming red-brown and thicker on exposure to air, and finally separating crystals of cinnamic acid. It has a strong, but agreeable, cinnamon odour, and a sweet, pungent, aromatic taste. The sp. gr. increases with the age of the oil. It remains clear at −10°, but at a lower temperature (−20°) separates a stearoptene. It is readily soluble in alcohol, but not in cold petroleum spirit, and when fresh is neutral to litmus, becoming acid by oxidation.

In addition to cinnamaldehyde, cinnamon oil contains small amounts of eugenol, phellandrene, methyl *n*-amyl ketone, pinene, cymene, furfural, benzaldehyde, nonylaldehyde, cuminaldehyde, caryophyllene, linalool, linalool *iso*butyrate, and hydrocinnamaldehyde (Walbaum and Hüthig, *J. pr. Chem.*, 1902, [ii], **66,** 47). Schimmel & Co. prepare an artificial cinnamon oil by mixing cinnamaldehyde with small quantities of these substances.

Some cinnamic acid may be present, the amount depending on the age of the sample, as the acid is produced by the oxidation of the aldehyde. The so-called "cassia stearoptene," described by Rochleder, is found only in old cassia oil. It is a complex aldehydic derivative. Cinnamyl acetate is sometimes present.

Schimmel has described (*Schimmel's Geschaftsber.*, Oct., 1914—Apr., 1915) a pale yellow oil with a strong odour of camphor, obtained from Japanese wild cinnamon bark in a yield of 1.7–2.1%. This has the sp. gr. 0.9245 at 15°, index of refraction n_D^{20} 1.4779, optical activity +8°.34, acid number 0.6 and ester number 14.8 It is soluble in one or more volumes of 80% alcohol. The chief constituent is camphor but terpenes and cymol seem also to be present.

Hirschsohn (quoted from *Phar. Zeit. f. Russl.*, 1891, **30,** 790; by Gildemeister and Hoffmann, "*Volatile Oils,*" p. 386) found that owing to the solvent action of cinnamic acid on lead, the oils are apt to become contaminated with that element from the leaden vessels in which they are often imported. As the oils are used for food flavours and sometimes in medicines for internal use the presence of lead is a danger.

The standard of purity required for cinnamon oil has been considerably modified by the latest edition of the British Pharmacopœia (1914). The latter states that oil of cinnamon is

> "Yellow when freshly distilled, gradually becoming reddish. Sp. gr. 1.000 to 1.030; optical rotation −0.5 to −1°; ref. index at 25° 1.565 to 1.580. Soluble in 3 to 4 parts of alcohol (70%). 1 drop dissolved in 5 c.c. of alcohol (90%) assumes a pale green, but not a blue or brown coloration, on the addition of 1 drop of T. Sol. of ferric chloride [5%] (absence of cinnamon leaf oil and cassia oil). Contains from 55% to 65% of cinnamic aldehyde as determined by the following test:
>
> To 10 c.c. of the oil add 70 c.c. of an aqueous solution (1 in 5) of sodium sulphite and sufficient solution of phenolphthalein to give a well-marked pink coloration. Heat the mixture on a water-bath, shake well and neutralise with acetic acid diluted with twice its volume of water; repeat the heating and neutralisation until no further pink coloration is developed, the time occupied being from 30 to 45 minutes The oily layer which separates on standing, cooled to 15°.5 measures not more than 4.5 or less than 3.5 c.c. (presence of 55%to 65% of cinnamic aldehyde.)"

According to the U. S. Pharmacopœia 1916, when 2 c.c. of oil of cinnamon or cassia are shaken in a test-tube with from 5 to 10 c.c. of purified petroleum spirit and the latter decanted, this liquid should be colourless and should not assume a green colour upon shaking it with an equal volume of (1 in 1000) copper acetate solution (absence of rosin).

The United States Pharmacopœia requires not less than 80% cinnamaldehyde, whilst the German Pharmacopœia puts the limit at 70%.

Cripps and Brown (*Analyst*, 1909, **34**, 519; 1910, **35**, 392) estimate the essential oils in spices (particularly carraway and cinnamon) by heating the latter at 150°–160° (in the case of cinnamon) in a current of air which is afterwards passed through a heated combustion tube, the carbon dioxide formed being absorbed and weighed in the usual way. The weight of carbon found multiplied by 100/80 gives the weight of cinnamon oil.

Adulterations of Oil of Cinnamon.—Oil of Ceylon cinnamon is liable to be adulterated with oil of cassia and oil of cinnamon leaves. The important data for detecting these are the amounts of eugenol and cinnamaldehyde. Parry found many samples of cinnamon oil in the London market which had been adulterated with a mixture of cinnamon-leaf oil and synthetic cinnamaldehyde added in large proportion to the genuine oil. He gives the following figures yielded by adulterated oils of this type:

Sp gr.	% Cinn ald.	% Eugenol
1 036	25 5	45
1 042	24 8	47
1 051	27 0	49

A qualitative test for eugenol is often of use. A drop of genuine cinnamon oil dissolved in 5 drops of strong alcohol produces a pale green with ferric chloride, but leaf oil produces a deep blue.

When the amount of cinnamaldehyde is low an estimation of the eugenol should be made. The most accurate method is that described by Thomas (*Ber. Pharm. Ges.*, 1891, **1**, 279). The oil is mixed in a beaker with 4 volumes of 15% sodium hydroxide solution and treated with excess of benzoyl chloride. Esterification takes place rapidly if the mixture is well stirred. After cooling, water is added and the crystals melted, washed with warm water, and dissolved in a small quantity of hot 90% alcohol. The solution is shaken whilst being cooled to 17°, so that the benzoyleugenol separates in small crystals. The latter are collected on a tared filter, washed with a small known volume of alcohol, dried at 101°, and weighed. A correction must be made for the amount of benzoyleugenol dissolved in the (90%) alcohol, 100 c.c. of which at 17° dissolve 2.20 grm.

Umney (*Pharm. J.*, 1895, [iii], **25**, 949) has suggested a simpler process, namely, to determine the diminution of volume resulting upon shaking the sample with a 5% solution of potassium hydroxide. The alkali dissolves some of the other constituents, but approximations can be made by the method. Adulteration may be assumed if the "eugenol content" is over 10%.

Hill has pointed out (*Chem. and Drug.*, 1910, **76**, 59) the value of a determination of the refractive index in detecting adulteration of cinnamon-bark oil. Of six samples of the genuine Ceylon oil of the finest quality, the ref. index at 25° varied only between 1.5727 and 1.5767 except for one sample which was more than 9 years old and was very resinous; this gave 1.5797. Two samples of cinnamon-bark oil distilled in England gave the values 1.5614 and 1.5752 respectively. The author gives values for other specimens and for cinnamon-leaf and cassia oils, cinnamic aldehyde, eugenol, pinene and phellandrene, which show that the genuine cinnamon-bark oil is distinguished from cassia oil and cinnamic aldehyde by a low sp. gr. (below 1.04 at 15°), a low ref. index (below 1.58 at 25°), a low aldehyde content (below 65%) and by affording a green colour with ferric chloride solution (cassia oil gives a chocolate brown colour). Adulteration with cinnamon-leaf oil can be recognised by an unduly high proportion of eugenol.

Pool (*Pharm. Weekblad*, 1903, **40**, 1101) states that the presence of 5% of oil of cloves can be detected in oil of cinnamon by means of Jacquemin's test. 1 c.c. of a dilute solution of aniline is treated with sodium hypochlorite solution until the liquid assumes a violet colour, when a drop of the oil is added. If the cinnamon oil is pure a dirty violet solution is obtained on shaking, which after diluting with water gives a clear violet filtrate, whilst in the presence of oil of cloves a green filtrate is obtained.

The oil of Chinese cinnamon, commonly known as *oil of cassia*, closely resembles the Ceylon product, except that its colour is deeper, its odour less delicate, its taste less sweet, and its sp. gr. somewhat higher—usually between 1.055 and 1.065. It is only slightly optically active, sometimes inactive. It should contain 70% cinnamaldehyde, and even then may not be of high quality, as good samples contain 75% or even 80%. In the London market the oil is graded by its aldehyde content, being sold as 70 to 75%; 75 to 80%; 80 to 85%.

A good cassia oil will contain not less than 75% of cinnamaldehyde. Only in rare instances does it rise above 90%. Gildemeister and Hoffmann ("*Volatile Oils*," p. 389) state that genuine oils from China have been noted in which the aldehyde content was below 50%, yet no adulteration could be recognised. The explanation of this could not be positively ascertained.

F. D. Dodge alone and in collaboration with A. E. Sherndal (*J. Ind. Eng. Chem.*, 1915, **7**, 1055–1056; 1918, **10**, 1005) has shown that oil of cassia contains cinnamaldehyde (75–90%), cinnamyl acetate, phenyl propylacetate, methyl *o*-coumaraldehyde, salicylaldehyde (0.1–0.2%), methyl salicylaldehyde, benzaldehyde, coumarin (about 0.3%), cinnamic acid (about 0.05%), an unidentified liquid acid and traces of salicylic and benzoic acids.

Oil of cassia is soluble in 3 to 4 volumes of 70% alcohol, and in all proportions of 90% alcohol. It gives a brown coloration with ferric chloride and forms a crystalline mass when shaken with an equal volume of nitric acid.

A rapid method of estimating lead has been described by O. F. Lubatti (*J. Soc. Chem. Ind.*, 1920, **39**, 35T). 5 c.c. of the cassia oil to be tested are diluted to 20 c.c. with 90% alcohol; 5 or 2.5 c.c. of this solution are taken for the estimation according as the lead-content is more or less than 0.025%, which will be estimated by a preliminary test. This amount is transferred to a 50 c.c. Nessler glass of small bore (2.5 cm.) by means of a pipette and diluted to about 20 c.c. with 90% alcohol. A blank from lead-free cassia oil, obtained by distilling the commercial oil, is prepared in a similar way. 1 c.c. of ammonium sulphide solution is added to both glasses and a standard lead solution (in 90% alcohol; 1 c.c. = 0.0001 grm. Pb) is added to the blank until the brown coloration produced matches the sample under examination, the liquid being stirred three times after each addition of standard solution by means of a piston-shaped glass rod. The results are calculated by means of the formula $x = n + 0.04/m$, where x is the percentage of lead sought, n the number of c.c. of standard lead solution required, and m the volume of original solution taken. The tint of the solutions can be compared by looking through the Nessler tubes resting on a white tile, but better results can be obtained by using a Dubosc colorimeter or an instrument described by the authors.

Adulterations of Oil of Cassia.—In the technical valuation of cassia oil, the cinnamic aldehyde is absorbed and the volume of the residue measured. Parry states (*Perf. Ess. Oil Rec.*, 1912, **3**, 46) that most of the cassia oil arriving in London at the present time (1912) is adulterated with resin. Consequently the unabsorbed portion of the oil obtained in the analysis has a much higher sp. gr. than cinnamic aldehyde so that an apparent content of 80% (by volume) of cinnamic aldehyde represents a considerably lower actual percentage by weight.

Adulterations of cassia oil, practised in former years with fatty oils, cedar-wood oil, and gurjun balsam, were easily detected, as the sp. gr. was lowered by the adulterants and the free solubility in 80% alcohol was prevented. Cedar-wood oil and gurjun balsam have a strong lævo-rotation.

Adulteration with a mixture of colophony and petroleum cannot be detected by these data. Schimmel & Co. (*Semi-annual Rep.*, Oct., 1889, 15; also "*The Volatile Oils*," Gildemeister and Hoffmann, p. 387) devised the following test for detecting this admixture:

50 grm. of cassia oil are weighed in a tared fractionation flask. A tube 1 metre long is attached as a condenser, and the oil is distilled with direct flame. At first, water passes off with crepitation, then the temperature rises rapidly to 240° and the bulk of the oil distils between 240° and 280°. When white fumes appear, indicating the beginning of decomposition of the residue, the distillation is stopped. The temperature may rise to 280° to 290° at this time. The flask is cooled and weighed. A good oil leaves a residue viscid and tough and not more than 10% of the original oil. The adulterated oil leaves a hard, brittle residue weighing more than 10%. The oil forms a clear solution with 70 to 80% alcohol. If petroleum is present, the mixture with such alcohol is turbid, and on standing some of the petroleum products separate.

Cassia oil that contains colophony and petroleum is soluble in 80% alcohol, but if only the latter is present the solution is turbid, the petroleum separating in oil drops. The following additional tests are taken from the work noted above:

Gilbert (*Chem. Zeit.*, 1889, **13**, 1406) suggests heating several grm. of the sample in a watch-glass in a drying oven at 110° to 120° to constant weight. He also states that the acid number is of value. An oil which upon distillation left 6% of residue had an acid number of 13. On adding 20% of colophony (having an acid number of 150) the acid number of the mixture was 40. An oil yielding 28% of residue had an acid number of 47.

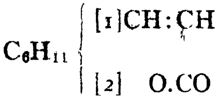
Hirschsohn (*Pharm. Zeit. f. Russl.*, 1890, **29**, 255) uses lead acetate as follows:

1 c.c. of the sample is added to 3 c.c. of 70% alcohol, and this is mixed, drop by drop, with a freshly prepared solution of lead acetate in 70% alcohol until the volume of the latter solution is half that of the oil solution. A precipitate shows colophony. Hirschsohn states that as little as 5% can be thus detected.

Oil of Cinnamon Leaves.—This is obtained by distilling the leaves of Ceylon cinnamon, but was at one time sold as oil of cinnamon root. Schimmel & Co. first pointed out the source. A product formerly sold as cinnamon-leaf oil has disappeared from commerce, and the true oil under its proper name has taken its place.

Oil of cinnamon leaves is a mobile, nearly colourless liquid, with an odour recalling both cloves and cinnamon. The sp. gr. ranges from 1.044 to 1.065. The oil has slight optical activity—sometimes negative, sometimes positive. The chemical composition is not clearly made out, but it contains eugenol and only a small amount of cinnamaldehyde.

COUMARIN,



$$C_6H_{11}\left\{\begin{array}{l}[1]\mathrm{CH{:}CH} \\ \qquad\qquad | \\ [2]\quad \mathrm{O.CO}\end{array}\right.$$

This is sometimes called "tonka-bean camphor." It is the odoriferous ingredient of tonka, the seed of several species of *Dipteryx*, and also occurs abundantly in the leaves of *Liatris odoratissima*. It occurs also in the leaves of several other plants. Coumarin forms colourless crystals, m. p. 67°, having an odour recalling that of vanillin but not so pleasant. It is very sparingly soluble in cold water, more so in cold alcohol (13 parts to 100 of alcohol at 16°); in hot alcohol it is freely soluble. It can be prepared synthetically by the interaction of sodium acetate, salicylic aldehyde. and acetic anhydride (Perkin, *Annalen*, 1868, **147**, 230).

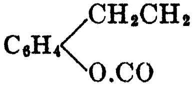
Kastle (see page 419) found that when the phenolsulphonic test for saccharin is applied to vanillin, the mixture becomes yellow and when the mass is heated to 160° for some minutes it becomes red and finally black. The solution of the mass in water becomes red on addition of sodium hydroxide. Coumarin gives no colour.

Coumarin is used in the preparation of perfumes, being mixed with other odoriferous principles, but its most important application from a practical analytical point of view is as an adulterant and substitute for vanillin (see under "Vanillin").

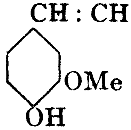
Estimation.—Obermayer (*Zeitsch. anal. Chem.*, 1913, 172) gives the following method of estimating coumarin in *Melilotus vulgaris* and *officinalis*. 10 grm. of the ground air-dried sample are extracted with ether in an extraction apparatus, and the ether is then evaporated in a 500 c.c. flask. The residue is treated with 300 c.c. of calcium chloride solution (1000 grm. in 3 litres) and distilled until the mass shows signs of solidifying. The heat should be regulated so that the operation lasts fully an hour. The distillate is diluted to a definite volume and then filtered. An aliquot portion of the filtrate is mixed with zinc sulphate solution, and then with excess of standard potassium permanganate solution and boiled on an asbestos plate for 10 minutes. After cooling, the liquid is filtered through an asbestos filter and the precipitate washed with water. The excess of permanganate in the filtrate and washings is estimated in the usual manner by titrating with oxalic acid. The titre of the permanganate solution is best verified by a check experiment with pure coumarin.

Coumaric Acids.—Hydroxycinnamic acids, $OH.C_6H_4.CH:CH.CO_2H$. 3 isomeric forms are, of course, known, respectively, 1–2, 1–3, and 1–4. The 1–2 form occurs in the leaves of species of *Melilotus* and in *Angræcum fragrans.* It can also be prepared by boiling coumarin with strong solution of potassium hydroxide or sodium ethoxide. It crystallises in colourless prisms, m. p. 208° (decomp.), which are freely soluble in water and alcohol. Solutions of alkali coumarates show a bright green fluorescence. By fusion with potassium hydroxide, 1–2 coumaric acid is converted into salicylic and acetic acids. By the action of nascent hydrogen it is converted into melilotic acid.

1–4 coumaric acid occurs in small proportion in red acaroid resin, partly free and partly as a complex ester, and in larger proportion in yellow acaroid resin. Esters of this acid are also found in Cape aloes and in the resin of *Picea vulgaris.* The acid can be obtained by hydrolysis of a glucoside *naringin,* which occurs in the blossoms of *Citrus decumana,* and may also be obtained by careful oxidation of 1–4 hydroxy-benzaldehyde.

Melilotic Acid.—1–2 hydrocoumaric acid, $OH.C_6H_4CH_2.CH_2(COOH)$, is obtained by the action of sodium amalgam on 1–2 coumaric acid or on coumarin. It occurs in association with coumarin in yellow melilot (*Melilotus officinalis*). It melts at 82° to 83° and produces a bluish tint with ferric chloride. It yields salicylic and acetic acids when fused with potassium hydroxide. When distilled alone, it is converted into its lactone or anhydride, *hydrocoumarin,*  $C_6H_4\left\langle\begin{matrix}CH_2CH_2\\O.CO\end{matrix}\right.$, m. p. 25°, b. p. 272°. It can be regenerated by boiling with water.

Ferulic acid, $C_{10}H_{10}O_4$, m-*methoxy*-p-*hydroxycinnamic acid,*



occurs in the resins of *Pinus Laricis* asafœtida, and opoponax. It can be isolated from asafœtida by mixing the alcoholic solution with an alcoholic solution of lead acetate. Lead ferulate is precipitated, which is decomposed by means of dilute sulphuric acid not in excess, the watery liquid is decolorised with animal charcoal and the acid and the crystalline residue taken up with hot alcohol and allowed to crystallise out.

Ferulic acid reduces Fehling solution, and gives a dark yellowish-brown precipitate with ferric chloride.

Ferulic acid is related to *umbellic* acid, the lactone or anhydride of which, "*umbelliferone*," "*hydroxycoumarin*," occurs in asafœtida and galbanum resins and in the bark of the *Daphne mezereum.*

AROMATIC BALSAMS

The aromatic "balsams" are such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid, and yield cinnamic or benzoic methyl or ethyl esters by dry distillation. The term "balsam" is misapplied to "Canada balsam" and "copaiba balsam," which are true turpentines and do not contain or yield benzoic or cinnamic acid.

The aromatic balsams of practical interest are gum benzoin, Peruvian balsam, Tolu balsam, and liquid storax. The first of these will be conveniently considered separately, and the others conjointly under the head of "Cinnamic Balsams."

Gum Benzoin.—Gum Benjamin. The greater part of the benzoin of commerce comes from the *Styrax benzoin*, a tree of the East Indies. Several varieties of the balsam are known of which the more important are: Siam and Sumatra benzoin (from the *S. benzoin*); Penang benzoin (probably from the *S. subdenticulata*), Palembang benzoin (source uncertain, but not from *S. benzoin*); Padang benzoin (source uncertain).

Siam benzoin is the finest variety and occurs in tears, or masses consisting of loosely agglutinated tears, yellow, reddish, or brown externally, and translucent, milk-white, or almond-like internally. It sometimes occurs in brownish lumps, which when broken present an amygdaloid appearance from the white tears imbedded in the darker resinous matter. Siam benzoin melts at 75°. This variety is never enveloped in cotton cloth.

Siam benzoin is mostly composed of a mixture of benzoresinol benzoate and siaresinotannol benzoate, the latter being the more abundant. Among other ingredients are cinnamyl benzoate, or benzyl benzoate (0.3%), vanillin (0.15%), free benzoic acid, which may be as high as 15%, and a small amount of impurities (Lüdy, *Arch. Pharm.*, 1893, **231**, 461. See also Reinitzer, *Zeit. angew. Chem.*, 1909, **22**, 1904). As a rule, cinnamic acid or cinnamic esters do not occur in Siam benzoin, which fact serves to distinguish it from the Sumatra and Penang sorts; but some observers report samples of Siam benzoin in which cinnamic acid or its esters exist.

Reinitzer states (*Arch. Pharm.* 1914, **252**, 341) that, in addition to the benzoates of benzoresinol and siaresinotannol, Siam benzoin contains the benzoate of a previously unknown resin-alcohol, *lubanol.*

In confirmation of Reinitzer, and contrary to the opinion of Lüdy, H. Lieb and A. Zinke find (*Monatsh. Chem.*, 1918, **39**, 219–230) that the resinol obtainable from Siam benzoin is different from that of Sumatra benzoin. Lüdy's "benzoresinol" was probably a mixture of *d*-sumaresinol with a small proportion of *l*-benzoresinol. Further work of these authors (*Monatsh. Chem.*, 1918, **39**, 627–639) seems to show that the *d*-sumaresinol and siaresinol characteristic of Sumatra and Siam benzoins respectively are in fact acids and accordingly named d-*sumaresinolic acid* and d-*siaresinolic acid.*

Later work of Reinitzer (*Arch. Pharm.*, 1921, **259**, 60–69) and of A. Zinke and J. Dzrimal (*Monatsh. Chem.*, 1920, **41**, 423–441) suggests that lubanol is identical with coniferyl alcohol.

It should leave practically no ash.

Sumatra benzoin has a weaker and less agreeable odour than that of Siam benzoin. It occurs in large rectangular blocks, marked with the impression of a mat and covered with a white linen cloth. When broken, few but large white tears are seen in it. It is generally composed of brown resiniform matter with numerous small white chips or pieces intermixed, which give it a granitoid appearance. The white portions melt at 85° and the darker portions at 95°.

Sumatra benzoin consists principally of a mixture of a small amount of benzoresinol cinnamate and much benzoresinotannol cinnamate. The remaining ingredients are free benzoic acid, styrol, traces of benzaldehyde, benzene, vanillin 1%, phenylpropyl cinnamate (about 1%), cinnamyl cinnamate (styracin) (2–3%) (Lüdy, *Arch. Pharm.*, 1893, **231**, 43).

The part soluble in ether when ignited leaves 0.01% ash.

Cinnamic acid, indicated by the production of an odour of benzaldehyde on heating the benzoin with chromic acid mixture, is said by Muter to be characteristic of the Sumatra product. He gives as specially distinctive characters of Siam benzoin: the production of a cherry-red benzoin when sulphuric acid is added to the residue left on evaporating the solution of the benzoin in petroleum spirit; the complete solubility of the sample in chloroform, but not in ether; and the lower m. p.

Palambang benzoin appears to be, in the main, similar to Siam benzoin in composition.

Padang Benzoin.— The composition of this is not well made out, but it seems to contain no cinnamic acid or ester thereof.

Penang benzoin closely resembles the Sumatra variety, but occasionally differs from it in colour, and more so in odour, which then suggests that of storax.

It contains cinnamic esters.

Qualitative Tests.—Gum benzoin always contains more or less bark and similar matters, and in inferior specimens these are present in very large proportion. With the exception of these impurities, benzoin should dissolve in 5 times its weight of alcohol. The resultant tincture from Siam benzoin has a distinct red colour, whilst that yielded by the other varieties is brown or yellowish-brown. On addition of water, the liquid becomes milky, and the odour peculiar to the particular variety is readily perceived. That of Siam benzoin is pleasantly balsamic and similar to vanilla; Penang benzoin often smells like storax; whilst the odour of Sumatra benzoin is fainter, less pleasant, and distinct from either of the former.

The presence of cinnamic acid may be recognised by the odour of benzaldehyde (bitter-almond oil), developed on adding potassium permanganate to the hot liquid obtained by boiling the benzoin with milk of lime and filtering. Or the tincture of benzoin may be treated with water, and the liquid, filtered from the precipitated resin, treated with a solution of permanganate or bleaching powder. Another method is to triturate the benzoin with lead dioxide and distil the mixture with water.

The British Pharmacopœia (1914) gives the following test for Sumatra Benzoin:

"When 0.5 grm. is slowly heated to about 40° with 10 c.c. of solution of potassium permanganate an odour of benzaldehyde is evolved (distinction from Siam benzoin). Not more than 15% insoluble in alcohol (90%). Ash not more than 5%."

The U. S. Pharmacopœia 1916 gives the following tests for both varieties of benzoin.

Heat gently 1–2 grms. of the benzoin with 15 c.c. of purified light petroleum and, after cooling, transfer the supernatant liquid to a separatory funnel, wash once with 10 c.c. of saturated sodium bicarbonate solution and then with water until free from bicarbonate: on the addition of 20 c.c. of copper acetate solution (1 in 200) and vigorously shaking the mixture no green colour is noticeable in the petroleum layer (absence of rosin and foreign resins).

Treat about 1 grm. of powdered benzoin with 15 c.c. of warm carbon disulphide, filter the solution, wash the filter with an additional 5 c.c. of carbon disulphide and allow the mixed liquids to evaporate spontaneously; not less than 12.5% of residue remains, which corresponds to tests for benzoic acid.

Sumatra benzoin does not yield more than 2.5% of ash.

Siam benzoin does not yield more than 2% of ash.

Not less than 75% of Sumatra and not less than 90% of Siam benzoins dissolves in alcohol; the alcoholic solution upon dilution with water become milky and is acid to litmus.

Analysis.—K. Dieterich (*Anal. d. Harze*, etc.) has devised a process applicable to benzoins in the commercial condition. This includes the estimation of ash and of data termed, respectively, "indirect acid value," "cold-saponification value," and "ester value." The last value is derived from the first two. The procedures are as follows: The weighed portions should be taken from a comparatively large amount of the material that has been finely powdered and well mixed.

Indirect Acid Value.—1 grm. is mixed in a flask with 10 c.c. of half-normal alcoholic alkali and 50 c.c. of 96% alcohol. The mixture is allowed to stand exactly 5 minutes, and then titrated with half-normal sulphuric acid and phenolphthalein until the solution is yellow, and a fresh portion of the indicator does not turn red on being dropped into the liquid, and the sodium sulphate separates readily. The supernatant liquid must be yellow. The c.c. of alkali neutralised by the sample, multiplied by the 28.08, gives the *acid value.*

Cold-saponification Value.—1 grm. of the sample is placed in a glass-stoppered flask with 20 c.c. of half-normal alcoholic alkali and 50 c.c. of petroleum spirit (sp. gr. 0.700). The flask, tightly closed, is allowed to stand for 24 hours at room temperature; after dilution with alcohol, the liquid is titrated with half-normal sulphuric acid and phenolphthalein. The c.c. of alkali neutralised, multiplied by 28.08, gives the cold-saponification value.

The ester value is the difference between the above data.

Dieterich gives the following as the limits of values with pure samples of the different benzoins:

	Siam	Sumatra	Palambang	Padang	Penang
Ash	0.03–1.5 %	0.0–1.5 %	1.1–4.02 %	1.07 %	0.38–0.77 %
Ind. A-V	140–170	100–130	113.4–130.9	121.8–124.6	121.8 –137.2
Cold-S-V	220–240	180–230	198–219.8	201.6–205.8	210–296.8
E-V	50–75	65–125	84–91	79.8–81.2	87.5–91.7
Sol. in 96 % alcohol	95 %	70–80 %	91 %	....	94 %

Dieterich found that the above data are more or less influenced by several of the usual adulterations of benzoin. Dammar and storax depress the acid value, turpentine depresses the cold-saponification and ester values; colophony depresses the acid value, but the effect is noticeable only when comparatively large amounts are present. For special tests for colophony, see under that substance.

The *Helfenberger Annalen* for 1903 (quoted by *Chem. and Drug.*, 1904) gives the following data from a sample of Siam benzoin, but the details of the methods used are not available:

Acid value	126.2
Ester value	96.4– 95.0
Saponification value	221.2–222.6
Ash	0.27%
Insoluble in spirit	3.6%

The estimation of the cinnamic acid may be approximately effected as indicated on page 434. As much as 11% has been found.

Gum benzoin often contains from 12 to 14% of benzoic acid, but occasionally 18 or 20% is reached. The proportion present may be ascertained by the following sublimation process: The sample is powdered, mixed with sand, and the mixture heated in a beaker or earthenware jar, furnished with a cap of thin filter-paper pierced with small holes. Over this is placed a cone or hood of stout paper. The benzoic acid sublimes and condenses on the inside of the hood, any oil and impurities being retained by the diaphragm of filter-paper.

Another method for the approximate assay of gum benzoin is to digest 10 parts of the powdered gum with 6 parts of slaked lime and

100 parts of water. After 6 hours, the liquid is boiled, filtered, and the residue washed. The filtrate is concentrated, rendered strongly acid with hydrochloric acid, and thoroughly cooled. The precipitated benzoic acid is filtered off, washed with a little water, and dried between folds of blotting-paper. The small quantity of acid retained in the mother liquor may be extracted by agitation with chloroform, and the residue left by the spontaneous evaporation of the chloroform may be added to the main quantity of benzoic acid. A preferable plan is to agitate the acidified liquid at once with chloroform, without filtering off the precipitated benzoic acid, and subsequently to recover the benzoic acid from its chloroform solution by the spontaneous evaporation of the solvent, assisted by a current of dry air from a bellows. If ether be substituted for the chloroform, the product will contain a small quantity of water and the estimation will be too high. In any case, the benzoic acid extracted by chloroform or ether from Siam benzoin will be liable to contain vanillin.

Cocking and Kettle (*Proc. Brit. Pharm. Conf.*, 1914, 13) give the following method to estimate balsamic acids. 5 grm. are extracted with alcohol in a Soxhlet apparatus and the extract hydrolysed with alcoholic potassium hydroxide. The alcohol is evaporated, the residue dissolved in 100 c.c. of water and treated with a slight excess of hydrochloric acid, 5 grm. of light magnesium oxide and 20 c.c. of xylene. The whole is boiled under a reflux condenser for an hour, cooled, the aqueous portion filtered off and the insoluble matter boiled twice with 100 c.c. of water, which is allowed to cool before filtering. The combined aqueous extracts are shaken out once with ether, then the balsamic acids are liberated by the addition of hydrochloric acid and removed by ether. The latter is distilled off, the residue dried in a vacuum over sulphuric acid and weighed. To estimate the cinnamic acid, the ethereal residue is left over-night in contact with excess of a 5% solution of bromine in carbon tetrachloride and the excess is driven off by evaporation on a water-bath. The residue is evaporated several times with ether dried as before and weighed. The amount of cinnamic acid is calculated from the increase of weight, one mol. of the acid absorbing two atoms of bromine.

The "free" balsamic acids are estimated by boiling the powdered drug with water, magnesium oxide and xylene and proceeding as above. The acid and ester values are determined on the alcoholic extract of a separate portion of the drug.

Tincture of Benzoin.—This is a simple solution of benzoin in alcohol of about 95%; usually the proportion is 1 of benzoin to 5 of alcohol. Compound tinctures are also used. For the compound tincture prepared according to the British Pharmacopœia it has been claimed that it will be of such strength that 10 c.c. will leave not less than 1.8 grm. of residue on evaporation. Owing to the volatility of some of the ingredients, it is difficult to evaporate to constant weight. E. Dowzard (*Chem. and Drug.*, 1904, **64**, 327) states that the following process will give good results:

2 c.c. of the sample are placed in a tared flat-bottomed nickel basin (diameter about 6 cm.); to this 0.1 grm. of recently ignited magnesium oxide in fine powder is added; the mixture is worked into a smooth condition with a small glass rod, which should be weighed with the basin. After allowing the mixture to stand for about 15 minutes, the alcohol is slowly driven off, stirring continually. The basin is then placed in a water-oven, and its contents dried at 99° to 100° for 4 or 5 hours. For drying purposes Dowzard uses an oven through which a slow current of dry air passes, a high vacuum being at the same time maintained. If an ordinary drying-oven is used, a longer time will be required than when using a vacuum apparatus. Before taking out of the oven, a cap of filter-paper perforated with small holes should be placed over the basin, as crepitation occurs on cooling. If, after the first weighing, a further drying is considered necessary, the perforated cap should be put over the basin before it is placed in the oven, and should not be removed until the moment before weighing; if this precaution is not taken, a slight loss may occur.

The weight of magnesium oxide used must, of course, be subtracted from the result. The benzoic and cinnamic acids are part of the total solids, and most important constituents of the tincture; they should therefore be fixed by chemical means before drying.

A large batch of this tincture, made on the manufacturing scale, was found to contain 19.4 grm. of extractive per 100 c.c. when tested by the above method, using magnesium oxide as a fixing agent. If the extractive from a compound tincture of benzoin is dried to a constant weight at 100°, the results will be from 2% to 2.5% below the actual amount of total solids present.

CINNAMIC BALSAMS

Under this description are included Peruvian balsam, tolu balsam, and liquid storax. These substances are all closely allied to one another, but in their physical properties and quantitative chemical composition, they present considerable differences.

The following table exhibits the more important distinctions between Peru and tolu balsams and storax:

	Peruvian balsam	Tolu balsam	Liquid storax
Botanical origin	*Toluifera Pereiræ.*	*Toluifera Balsamum.*	*Liquidambar orientalis.*
Geographical origin	San Salvador, Central America.	Colombia, Turbace, Tolu, and Venezuela.	Asia Minor.
Consistency and appearance.	Viscid, but not glutinous, dark brown liquid, resembling molasses; transparent and reddish-brown in thin layers Gradually thickens on exposure.	When fresh, yellow transparent, and liquid; changing rapidly to reddish-brown, and becoming solid and friable or brittle; but softening between the teeth, and readily fusing. Such samples have a granular crystalline structure; and crystals of cinnamic acid are visible under the microscope.	Brownish-yellow or greyish, viscous liquid. Under the microscope shows globules of water, tabular crystals of cinnamic acid, and frequently feathers of styracin.
Taste.	Bitter and persistently irritating.	Sweetish, aromatic, and somewhat irritating.	Pungent and balsamic.
Odour.	Agreeable.	Aromatic; more apparent on warming.	Sweetish or strong and oppressive.

The cinnamic balsams are closely allied, consisting essentially of the benzyl and cinnamyl esters of benzoic and cinnamic acids, mixed with resinous oxidation products of these esters, free benzoic and cinnamic acids, and the hydrocarbon cinnamene. The leading or characteristic constituents of Peru balsam may be said to be the cinnamein or benzyl cinnamate and styracin or cinnamyl cinnamate. Free benzyl alcohol is also present. In tolu balsam, on the other hand, the proportion of resin is large; but of the esters benzyl benzoate predominates, and cinnamyl benzoate and cinnamate exist in but small proportions. In liquid storax of Mexican origin, phenylpropyl cinnamate exists in considerable quantity together with 2 isomeric alcohol-like substances called α- and β-storesinol, to which the formula $C_{36}H_{55}.(OH)_3$ is attributed (*Ber.*, 1876, **9**, 274), and the cinnamic esters of these substances.

In some cases the substances obtained from the cinnamic balsams have been decomposition products of the methods of analysis. The following method may be adopted for the recognition of the principal constituents of aromatic balsams: The substance is dissolved in 2 or 3 parts of ether, and filtered from any insoluble matter. The solution is agitated with an equal volume of normal sodium hydroxide, the alkaline liquid withdrawn, and the agitation repeated with a fresh quantity of solution. If desired, the total acidity of the balsam can be deduced from the titration of an aliquot part of the alkaline liquid. The ethereal layer is then washed with water, and distilled at a gentle heat, the residue of neutral esters, etc., being weighed. The residue is then fractionally distilled.

The first fraction will contain any *cinnamene* which may be present, the next being rich in *benzyl alcohol*, which may be extracted by agitation with water and will yield benzaldehyde and benzoic acid by oxidation. *Cinnamyl alcohol* and *benzyl benzoate* pass over next, and at a higher temperature *benzyl cinnamate* and *cinnamyl benzoate* and *cinnamate* may be obtained. These esters suffer more or less decomposition unless the distillation is conducted *in vacuo*, and hence the last fractions consist largely of cinnamic acid, which can be removed by agitating the distillate with sodium carbonate solution. The alkaline liquid separated from the ethereal solution should be saturated with carbon dioxide, which precipitates much *resin*. The liquid is filtered, concentrated, and treated with hydrochloric acid, when a bulky precipitate is obtained representing the *free benzoic* and *cinnamic acids* of the balsam. These substances may be identified by their ordinary reactions. For their approximate separation, one half of the precipitate may be boiled with milk of lime and the liquid filtered and allowed to become cold, when the sparingly soluble calcium cinnamate is deposited in shining needles, the more soluble benzoate remaining in solution. The methods indicated on page 497 may also be utilised for the separation of the 2 acids. When an exact estimation of the free acids of a balsam is desired, it is better to agitate the ethereal solution with sodium carbonate instead of sodium hydroxide, as the latter reagent is liable to cause some decomposition of the esters.

Except for purposes of research, it is rarely necessary to make such an analysis of a balsam as is indicated above.

PERUVIAN BALSAM

White Peru balsams have been described by Biltz (*Chem. Zeit.*, 1902, **26**, 436), Thoms and Biltz (*Zeit. Oesterr. Apoth. V.*, 1904, **42**, 943), and by Hartwich and Hellström (*Arch. Pharm.*, 1905, **243**, 218).

Peruvian balsam is readily soluble in all proportions in absolute alcohol, glacial acetic acid, chloroform, acetone, and ethyl acetate; with an equal bulk of alcohol and ether it yields a clear solution, which on further addition of the solvent becomes turbid and deposits resin. Diluted alcohol takes up only a small proportion of the balsam. Cold ether and petroleum spirit dissolve it partially.

Cold petroleum spirit only dissolves the cinnamein and cinnamic acid of the balsam, but, on employing the hot solvent, styracin is also dissolved and is deposited in crystals on cooling. Carbon disulphide acts in a characteristic manner. Agitated with three times its weight of the cold solvent, the greater part of the balsam is dissolved to a colourless or slightly coloured liquid, from 10 to 16% remaining as a reddish-brown, sticky liquid, adhering firmly to the sides of the glass, whilst the solution may be readily poured off.

Analysis.—The investigations of Dieterich (*Anal. d. Harze.*, etc.) have shown that many of the commonly accepted tests for purity of this balsam have no value. He gives the following methods as of service:

Direct Acid Value.—1 grm. of the sample is dissolved in 200 c.c. of alcohol (96%) and titrated with decinormal alcoholic alkali, using phenolphthalein. The c.c. of alkali required multiplied by 5.616 gives the direct acid number.

Cold Saponification Value.—The procedure is mainly as given under "Benzoin," using 1 grm. of the sample in a 500 c.c. glass-stoppered flask with 50 c.c. of petroleum spirit (sp. gr. 0.700) and 50 c.c. half-normal alcoholic alkali. After standing 24 hours at room temperature, 300 c.c. of water are added, well shaken, until the separated dark alkali salt has been dissolved, and the solution titrated, with continuous agitation, with half-normal sulphuric acid in the presence of phenolphthalein. The c.c. of alkali neutralised by the sample, multiplied by 28.08, gives the cold saponification value.

The *ester value* is obtained by subtracting the direct acid value from the cold saponification value.

Ether Insoluble Matter.—This is obtained by Dieterich by adding warm ether in small portions to a weighed portion of the sample until a portion of the solvent no longer leaves any residue on evaporation. The undissolved portion is then weighed. It will probably be better to extract in a Soxhlet tube.

Aromatic and Volatile Ingredients.—The ethereal extract is shaken with 20 c.c. of a 2% sodium hydroxide solution, separated and evaporated at room temperature until no odour of ether is perceptible. The residue is placed for 12 hours in the desiccator, weighed, placed for a second 12 hours in the same and weighed again. The mean between these 2 weights is taken as the datum for fixed matter from which the volatile matter can be calculated.

To estimate cinnamein Lehmann and Müller recommend (*Arch. Pharm.*, 1912, **250,** 1) the following method. 5 grm. of water are mixed with 2.5 grm. of the balsam in a 75 c.c. bottle, 30 c.c. of ether are added and the mixture shaken for 1 minute. 5 grm. of sodium hydroxide solution are then added and the mixture again shaken for 1 minute. The bottle is securely corked and set aside bottom upwards for 10 minutes. The cork is then carefully loosened and the aqueous portion allowed to run away till only 3 c.c. are left. 0.5 grm. of gum tragacanth is then added to the contents of the bottle and the whole shaken. After 5 minutes the clear ethereal solution is run into a tared wide-mouthed flask and its weight (w) noted. The solvent is then distilled off, the residue dried at 100° for 30–45 minutes and its weight (w') determined. The percentage of cinnamein (x) in the balsam is given by the following equation: $x = (30w'/w - w')40$. In this method the device of running most of the alkaline solution out of the inverted bottle is criticised as impractical by Frommé (*Caesar and Loretz Jahres-Ber.*, 1912, 20) who recommends fixing all the solution with gum tragacanth.

According to E. C. Merill (*J. Assoc. Off. Agric. Chem.*, 1919, **3,** 194–197), the Hanuš method is unreliable for estimating the iodine value of the cinnamein separated from Peru balsam, the time of contact (30 minutes) usually employed is too short, at least 3 hours being required. There is no marked difference in viscosity between true and artificial Peru balsam. Cinnamein from artificial balsam has a slight optical rotation ($+ 0°.35$ for 2 c.c. of cinnamein dissolved in 10 c.c. of benzene in a 100 mm. tube) and the refractive index n_D^{15} is less than 1.57, whilst cinnamein from genuine balsam is optically inactive and has n_D^{15} greater than 1.57.

For the iodine value of the cinnamein from reliable Peru balsam Jensen found (*Pharm., J.*, **90**, 210) the values 23.8 and 25.5 as against 1.5 for the synthetic ester. Upon fractional distillation of the cinnamein, the first 30% is optically active when derived from the true balsam, but inactive when obtained from the synthetic ester. This author states that benzyl benzoate has sp. gr. 1.121, saponification value 264.1, whilst for benzyl cinnamate the values are 1.098 and 235.3, respectively.

Esters of Resin Acids.—The alkaline solution separated from ether by the action of the alkali, as noted in the last paragraph, is rendered acid by dilute hydrochloric acid, filtered through a tared filter and washed by the aid of a filter pump with as little water as possible until the washings are free from chlorides. The residue dried at 80° to constant weight is taken.

With these processes, Dieterich obtained from commercial samples the following range of data:

Sp. gr.	1.135	1.145
Direct acid value	60.0	80.0
Cold saponification value	240.0	270.0
Ester value	180.0	200.0
Resin esters	20.0%	28.0%
Aromatic and volatile ingredients	65.0%	77.0%
Ether insoluble	1.5%	4.5%

From authentic pure specimens from Honduras the following figures were obtained:

	I	II	III
Direct acid value	77.4	76.9	77.3
Cold saponification value	241.0	214.3	215.0
Ester value	165.6	137.4	137.6
Resin esters	15.7%	13.2%	17.3%
Aromatic and volatile ingredients	71.4%	77.5%	73.6%
Ether-insoluble	4.4%	4.3%	3.5%

The British Pharmacopœia 1914 gives the following description and method of analysing Peruvian balsam:

"Insoluble in water; soluble in chloroform. 1 volume is soluble in 1 volume of alcohol (90%), but on the further addition of 2 or more volumes of alcohol, the whole becomes turbid. Sp. gr. between 1.140 and 1.158. Does not diminish in volume when shaken with an equal bulk of water (absence of ethylic alcohol). When tested by the following method it yields not less than 57% of cinnamein, the saponification value of which is not less than 235.

"Dissolve 1 grm. of the balsam in 30 c.c. of ether and shake in a separating funnel with two successive quantities of 20 c.c. and 10 c.c. of N/2 solution of sodium hydroxide. Separate the alkaline solutions, mix and shake with 10 c.c. of ether. Add the second ethereal solution to that previously obtained. Wash the mixed ethereal solutions with two successive quantities of 5 c.c. of water. Transfer the ethereal solution thus washed to a tared wide-mouthed flask, evaporate at a gentle heat until the odour of ether has disappeared, add 1 c.c. of absolute alcohol, dry at 100° for half an hour and weigh. The weight of the cinnamein thus obtained is not less than 0.57 grm. To this residue add 20 c.c. of N/2 alcoholic solution of potassium hydroxide, and 20 c.c. of alcohol (90%). Attach a reflux condenser, boil for half an hour, and titrate back with N/2 solution of sulphuric acid, solution of phenolphthalein being used as indicator. Each grm. of the residue thus treated requires not less than 8.4 c.c. of the alkaline solution for complete saponification (corresponding to a saponification value of not less than 235) "

According to the U. S. Pharmacopœia 1916 Peru balsam should answer to the following tests:

" 1 grm. of the balsam forms a clear solution when shaken with a solution of 3 grm. of hydrated chloral in 2 c.c. of distilled water (absence of fixed oils). Shake about 1 grm. of the balsam with 5 c.c of purified petroleum spirit and warm the mixture on a water bath for 10 minutes adding a sufficient quantity of the solvent to replace the loss by evaporation. On evaporating 2 c.c. of the petroleum solution no odour of turpentine is noticeable, and when the residue is treated with a few drops of nitric acid, no green or bluish colour is produced (absence of turpentine or rosin). Weigh accurately about 1 grm. of the balsam and dissolve it in 100 c.c. of alcohol, add 1 c.c. of phenolphthalein solution and titrate the solution with N/2 potassium hydroxide solution. The acid number thus obtained is not less than 56 nor more than 84.

Mix about 3 grm of the balsam accurately weighed, with 30 c.c. of sodium hydroxide solution and shake the mixture for a few minutes with 60 c.c. of ether. Then add about 3 grm. of powdered tragacanth, filter and transfer 50 c.c. of the ethereal filtrate (representing 5/6 of the weight of the balsam taken) into a tared conical flask. Evaporate the ether and dry the residue to constant weight at 100°. The weight of the residue of cinnamein so obtained is not less than 50% nor more than 56% of the weight of balsam represented by the ethereal solution (50 c.c.) taken. Dissolve the residue in 25 c.c. of alcohol, add 25 c.c. of N/2 potassium hydroxide solution and heat the mixture carefully in a flask provided with a reflux condenser, during half-an-hour, on a water-bath. Then add 1 c.c. of phenolphthalein solution and titrate the excess of alkali with N/2 hydrochloric acid solution. The amount of N/2 potassium hydroxide solution consumed corresponds to a saponification value for the cinnamein of 235 to 238."

The German Pharmacopœia regulation is satisfied if the 56% of cinnamein is obtained by three successive extractions with ether, but it must require at least 23.66% of potassium hydroxide for hydrolysis, and the balsam must have a cold saponification value not less than 224.6.

According to Stocker (*Apoth. Zeit.*, 1911, **26**, 283) there are undoubtedly pure and genuine balsams on the market which will not dissolve (1 grm.) to a clear solution in a solution of 3.0 grm. of chloral hydrate in 2 grm. of water. He suggests that the test should be modified by using 3.5 grm. of chloral hydrate.

Adulterations of Peruvian Balsam.—Peruvian balsam is liable to adulteration with the cheaper cinnamic balsams (tolu and storax); copaiba and gurjun balsams; colophony; an alcoholic solution or extract of gum benzoin; alcohol; and even with fixed oils, especially castor oil. Hence the examination of Peru balsam for the detection of these adulterants is of some importance. Many of the usual adulterants of balsam have a lower sp. gr. than the genuine substance, which varies in density between very narrow limits, 1.150 being the maximum and 1.137 the extreme minimum. Any sample having a lower density than 1.138 should be regarded with suspicion.

The presence of *alcohol* is indicated by the loss of volume undergone by the balsam on agitating with water. Small quantities may be detected by distilling the sample with water and sodium carbonate and examining the distillate by the iodoform and chromic acid tests.

According to Rosenthaler (*Zeit. anal. Chem.*, 1905, **44**, 292), pure Peru balsam, when treated with a solution of vanillin in hydrochloric acid, gives no coloration, but if it is adulterated with 5% or more gurjun balsam, a purple-red and then a violet colour is produced, whilst in the presence of 10% of copaîba balsam the colour is faint violet.

K. Dieterich (*Ber. pharm. Ges.*, 1908, **18**, 135) states that adulteration with 30% of tolu balsam can be detected by the following test: A small quantity of the balsam is dissolved in ether, and to the solution a little concentrated sulphuric acid is added to form a lower layer. Hydrochloric acid is then cautiously added so that 3 strata are formed. With genuine Peru balsam the upper and lower strata are red and the intermediate hydrochloric acid is colourless. Tolu balsam imparts a very characteristic green colour to the upper ethereal layer.[1]

The artificial Peruvian balsam known as "Perugen," when shaken with 5 volumes of petroleum spirit and the extract evaporated, gives a residue, which when treated with a little nitric acid (sp. gr. 1.38) acquires an olive-green colour. The residue from the natural balsam becomes golden-yellow when similarly treated. (Cæsar and Loretz, *Pharm. J.*, 1905, [iv], **21**, 579.)

According to the United States Pharmacopœia, the petroleum spirit extract of Peru balsam, when shaken with an equal volume of copper acetate solution (1: 1,000), should not become green or bluish-green (absence of resin, turpentine, storax, fatty oils, etc).

L. van Itallie found (*Amer. J. Pharm.*, 1921, **93**, 24–26) a sample of Peru balsam adulterated with methyl phthalate. He states that benzoyl benzoate is also used as an adulterant, and that both esters may be detected by Dietrich's test.

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[1] Perrot and Goris, however, state that the pure Peru balsam gives this reaction.

K. Dieterich (*Ber. deuts. Pharm. Ges.*, 1913, **23**, 622) has examined samples of genuine Peru balsam which gave the following values: sp. gr. at 15°, 1.160; acid value 74.02–76.92; saponification value 214.34–243.07; iodine value 22.07 to 25.87; cinnamein 56.56–77.56% saponification value of the cinnamein 253.61; iodine value of the cinnamein 7.48–7.91; resin esters 24.95%; and insoluble in ether 2.45–4.38%. The results obtained from artificial and "synthetic" balsams, as a whole, differed considerably from these limits, although individual values were frequently normal. The author finds that only the following identification tests are distinctive: Hager's petroleum spirit test, determination of solubility in alcohol, chloroform, chloral hydrate and carbon disulphide; the nitric acid test; the zone reactions and the qualitative tests of the Swiss Pharmacopœia. He gives the following new colour test. 1 drop of the sample is shaken with 5 c.c. of petroleum spirit, and about half the liquid poured off. The remainder is mixed with 5 c.c. of ether and shaken with a few drops (10 to 15) of sulphuric acid, added drop by drop, when genuine Peru balsam gives a violet to blue coloration, whilst artificial products give quite different colours. This reaction is due to the cinnamein of the balsam.

When distilled in a current of steam, Peru balsam yields (Dieterich) (*Ber. deuts. Pharm. Ges.*, 1914, **24**, 225) about 5% of a thick yellowish oil having an odour like that of the original material. In this way volatile adulterants can be detected. For the oil from the genuine balsam Sortell (*Ber. deuts. Pharm. Ges.*, 1914, **24**, 233) describes the following characters: sp. gr. 1.0869 at 17°, saponification value 245.7, $[\alpha]_D + 1.876°$. After saponification the oil had sp. gr. 1.002 and $[\alpha]_D + 4°$ at 20°, and it was found to contain benzyl alcohol and peruviol, the greater part of which distilled at 98°/16 mm. Benzoic and cinnamic acids were products of the hydrolysis.

Dieterich (*Ber. deuts. Pharm. Ges.*, 1914, **24**, 225) states that irregularities in the preparation of a genuine balsam may cause abnormal colorations in the nitric acid and zone tests.

From his analyses of genuine and adulterated balsams, Dieterich concludes that adulterations usually raise the direct acid value and lower the cold saponification value.

A low ester-number indicates adulteration; if below 100 it suggests colophony, tolu balsam, or benzoin.

The matter insoluble in ether has a sorting value, but is of no use in detecting common adulterations.

In commercial samples the proportion of cinnamein ranged from 65 to 75%, and of resin esters 20 to 28% that is, a ratio of 1 of the latter to 3 of the former. Ratios, therefore, of 1 to 2 or 1 to 5 indicate much adulteration.

In valuing a sample, a high content of cinnamein is preferable to high content of resin esters.

TOLU BALSAM

This is from a leguminous plant, *Myroxylon toluifera*, growing in the northern portion of South America. In fresh condition the balsam is brownish-yellow, transparent in thin layers, and non-crystalline, but in time becomes hard, crystalline, and darker. The odour is aromatic and pungent. The m. p. ranges from 60° to 65°. It dissolves in alcohol, chloroform, and in watery solutions of alkalies. The alcoholic solution is acid to litmus.

The constituents of tolu balsam are not fully known, but it appears to consist principally of the following ingredients:

(1) An oily portion, benzyl benzoate with a little benzyl cinnamate; (2) cinnamic and benzoic acids; (3) vanillin; (4 toluresinotannol benzoate and cinnamate. Of these (4) is the most abundant; (1) forms about 7% (2) from 12 to 15%; (3) only traces. About 3% of impurities of various kinds are present.

By steam distillation on a large scale, a small amount of a volatile oil of pleasant odour can be obtained. This has a sp. gr. ranging from 0.945 to 1.090, slight optical activity, sometimes positive, sometimes negative, and contains phellandrene.

The following description of tolu balsam is given in the British Pharmacopœia, 1914.

> "Soluble in alcohol (90%) the solution being acid to litmus. Acid value 107.4 to 147.2; saponification value 170 to 202. If 5 grm. are gently warmed with three successive quantities of 25, 15, and 10 c.c. of carbon disulphide, the solution yields when evaporated to dryness a distinctly crystalline residue which when tested as described under 'Styrax Præparatus' yields not less than 1.25 grm. of balsamic acids."

According to the U. S. Pharmacopœia 1916 tolu balsam should give the following tests.

Shake about 1 grm. of the balsam with 25 c.c. of carbon disulphide, allow it to stand for 30 minutes, filter the liquid and evaporate 15 c.c. of the filtrate to dryness. The residue thus obtained when dissolved in glacial acetic acid does not show a green colour on the addition of a few drops of sulphuric acid (absence of rosin). The remaining portion of the filtrate when shaken with an equal volume of an aqueous solution of copper acetate (1 in 1,000) does not acquire a green colour (absence of rosin or copaiba). Dissolve about 1 grm. of the balsam, accurately weighed, in 50 c.c. of alcohol, add 1 c.c. of phenolphthalein solution and titrate the solution with N/2 alcoholic potassium hydroxide solution. The acid number thus obtained is not less than 112 nor more than 168. Now add sufficient N/2 alcoholic potassium hydroxide solution to the neutralised liquid to make the total volume of volumetric alkali solution exactly 20 c.c.; heat the liquid on a water-bath for half an hour under a reflux condenser and allow it to cool. Mix this liquid with 200 c.c. of distilled water or more if necessary and titrate the excess of potassium hydroxide with N/2 sulphuric acid solution. The total amount of N/2 potassium hydroxide solution consumed corresponds to a saponification value of not less than 154 nor more than 220.

Analysis.—The assay of tolu balsam usually includes the determination of the *direct acid value*, the *cold saponification value*, the *ester value*, the *matter soluble in ether*, the *volatile matter*, and the *esters of resin acids*, according to Dieterich's directions for Peru balsam.

The United States Pharmacopœia requires an acid number 112 to 168 whilst the German Pharmacopœia sets the limits at 112.3 to 168.4.

The following method of analysis is recommended by Delphin (*Svensk. Pharm. Tidskr.*, 1907, 3, 415): 2 grm. of the sample are dissolved as completely as possible in 5 c.c. of ether contained in a separating funnel. To the solution 20 c.c. of ether and N-potassium hydroxide solution are added and the mixture carefully shaken. After separation the aqueous layer is run into a 75 c.c. flask, the ethereal liquid washed with 2 c.c. of water, and the washings added to the aqueous portion. The ethereal extract is transferred to a tared Erlenmeyer flask and evaporated on a water-bath. After heating the residue on the water-bath for 30 minutes it is exposed over sulphuric acid for 12 to 18 hours and weighed, this giving the cinnamein. The alkaline aqueous liquid is treated with sodium hydrogen carbonate (2 grm.) until an abundant yellowish-white precipitate is formed, and then the liquid is submitted to a stream of carbon dioxide for an hour. The solution is filtered, and the precipitate washed with warm water until the wash-water is no longer alkaline. For the estimation of the resin esters the precipitate is dried to constant weight. The filtrate from the resin esters is treated with 6–7 c.c. of 25% hydrochloric acid. After effervescence has ceased the resin acid is collected on a tared filter, washed with boiling water until the filtrate is free from acid, dried and weighed. The cooled filtrate, in which the cinnamic acid will have crystallised, is extracted first with 40 c.c., then with 20 c.c. of ether. The combined ethereal extracts are titrated with N/10 potassium hydroxide solution (1 c.c. corresponds to 0.0148 grm. of cinnamic acid) in the presence of phenolphthalein.

A good balsam should contain not less than 8% of cinnamein and 25% of cinnamic acid, nor more than 1 % of resin acid.

Fleissig states (*Schweiz. Wochschr.*, 1911, **47**, 365) that one of the identity tests of the Swiss Pharmacopœia in which it is directed to treat the substance with alcohol 1:10, should be modified to read specifically 10% ethyl alcohol. Tolu balsam is readily soluble in 95% alcohol. Owing to emulsification there is some difficulty in determining the saponification and acid values. For the latter Merck recommends the following method: 1 grm. of the balsam is dissolved in 50 c.c. of alcohol; 6 c.c. of N/2 potassium hydroxide solution are added, then a few drops of phenolphthalein solution and, after shaking, 200–300 c.c. of water; the excess of alkali is titrated with N/2 hydrochloric acid. The number of c.c. of alkali solution used up by the balsam × 28 gives the acid value. The saponification value is determined by dissolving 1 grm. of the balsam in 50 c.c. of alcohol, adding 20 c.c. of N/2 alcoholic potassium hydroxide and heating for half an hour on a water-bath. Then 200–300 c.c. of water are added and the solution titrated with N/2 acid. The number of c.c. of alkali consumed in the saponification × 28 gives the saponification value.

T. T. Cocking and J. D. Kettle state (*Pharm. J.*, 1918, **101**, 40–41) that the most satisfactory method for the analysis of tolu balsam is to separate the aromatic acids by boiling with magnesium oxide and water, in the presence of a little xylene to soften the resinous matter. The magnesium salts of the aromatic acids are readily soluble in cold water, those of the resin acids being insoluble. For the estimation of the free balsamic acids, 5 grm. of the balsam are dissolved in 25 c.c. of hot alcohol, 5 grms. of light magnesium oxide and 20 c.c. of xylene are added and the contents of the flask well mixed. Then 100 c.c. of water are introduced and the mixture boiled under a reflux condenser for an hour. After cooling, the whole is poured on a Buchner filter, the aqueous portion of the filtrate is separated and the xylene together with the magnesia and the filter paper is returned to the flask. Boiling with 100 c.c. of water each time is repeated twice more, the mixed aqueous filtrate is washed once with ether, then acidified with hydrochloric acid, the aromatic acids extracted with 20 c.c. of ether and dried in vacuo over sulphuric acid. For the total balsamic acids 2.5 grm. of the balsam are saponified by boiling with alcoholic potash, the greater part of the alcohol is evaporated off, the residue is dissolved in 100 c.c. of hot water and acidified with hydrochloric acid. To the solution 5 grm. of light magnesium oxide and 20 c.c. of xylene are added and the mixture treated as before. The proportion of cinnamic acid in the balsamic acids is estimated by the gain in weight on bromination. For the determination of the acid value of tolu balsam, 5 grm. of the sample are dissolved in about 50 c.c. of boiling alcohol, a large amount of phenolphthalein solution (3–4 c.c.) is added and the hot solution is titrated with N/1 alcoholic potassium hydroxide solution until the colour becomes dark brown but not red. It is then boiled under a reflux condenser for a few minutes to break up the precipitate and the titration completed. With a large range of samples the authors found for acid value 92.2 to 132.4, for ester value 59.3 to 90.9, for saponification value 154.8 to 208 and for total balsamic acids 32.66–47.56.

Adulteration of Tolu Balsam.—The common adulterant is colophony, but when the balsam is high in price other substances (*e. g.*, copaiba) may be used.

For the detection of colophony qualitatively the Storch-Morawsky test (see under "Colophony") may be used.

The following test for colophony is described by Hirschsohn (*Pharm. Zeit. f. Russ.*, 1895, **34**, 497): The balsam is extracted with 4 to 5 volumes of petroleum spirit and the extract shaken with an equal volume of copper acetate solution. The production of a green coloration in the petroleum layer indicates the presence of colophony. Perrot and Goris recommend a similar test (*Bull. Sci. Pharm.*, 1908, 636).

The solubility in carbon disulphide has been proposed as a test and in the British Pharmacopœia of 1898 is given as follows:

5 grm. of the sample are extracted with 25 c.c. and then 10 c.c. of warm carbon disulphide. Upon evaporating the mixed solutions, the residue should require not less than one-third of its weight of potassium hydroxide for saponification, thus indicating a sufficient amount of cinnamic and benzoic acids in the sample.

Some good authorities are, however, not inclined to rely on this test, and much further study of this balsam is needed. K. Dieterich says that little if any pure tolu balsam is on the market. He gives the following data obtained by E. Dieterich, with which his own figures correspond, but the latter are not specially quoted:

Direct acid value	114.8–158.6
Saponification value	155.3–187.4
Ester value	31.2–40.5
Solubility:	
Alcohol (90%)	wholly soluble.
Ethyl acetate	wholly soluble.
Chloroform	almost wholly soluble.
Ether	53.2–87.9%
Benzene	82.2–nearly 100%
Petroleum spirit	2.2–10.7%
Oil of turpentine	27.8–54.5%
Carbon disulphide	19.6–88.1%

Syrup of Tolu Balsam.—Commercial syrup of tolu balsam is prepared either (1) by the British Pharmacopœia official method; (2) by precipitating an alcoholic tincture, or (3) by admixture with a distillate of the balsam.

According to Astruc and Cambe (*J. Pharm. Chim.*, 1903, [vi], **17**, 367), only the syrup prepared by the official direct maceration method liberates iodine from potassium iodide solution. Both the official syrup and that prepared from the tincture give a marked yellowish-green colour in the presence of excess of alkali. But the preparation from the distillate of tolu balsam gives neither of these reactions.

LIQUID STORAX

This is the product of *Liquidambar orientalis* of Asia Minor, and of *Liquidambar styraciflua* of America. It is a brownish-yellow or greyish viscous liquid, the better qualities of which possess a sweet, vanilla-like odour. Inferior specimens contain impurities which render the odour oppressive and disagreeable.

The taste is pungent and balsamic. Under the microscope globules of water and crystals of cinnamic acid and styracin are visible.

Oriental storax (from *Liquidambar orientalis*) contains styrene, $C_6H_5.CH:CH_2$, cinnamic acid styracin (cinnamyl cinnamate), $C_9H_9C_9H_7O_2$), phenyl-propyl cinnamate, ethyl cinnamate, vanillin, ethyl-vanillin; α- and β-storesin, $C_{35}H_{55}(OH)_3$, an amorphous resin, traces of benzoic acid and storesinol cinnamate. According to

Tschirch, benzoic and cinnamic acids are never found in the same specimen of oriental storax.

According to M. Heuze (*Ber.*, 1916, **49**, 1622–1632) Tschirch and van Itallie's storesinol cinnamate contains at least five and possibly six distinct substances. The major portion of the resin consists of two isomeric acids $C_{20}H_{30}O_2$ identical with abietic and pimaric acids, the chief components of the conifer resins.

Storesinol has the formula $C_{16}H_{25}O(OH)$, and its cinnamic ester is present to the extent of about 35% in the balsam.

American storax is known also as *sweet gum*, and, according to Harrison and Maisch (*Arch. Pharm.*, 1875, **206**, 545), it is identical with oriental storax; but this is improbable. It contains styracin, phenylpropyl cinnamate and storesin; but not ethyl or benzyl cinnamate. Styrene and traces of vanillin are probably present.

Qualitative Tests.—When treated with strong alcohol, ether, or chloroform, liquid storax dissolves, but generally leaves some mechanical impurities. With an equal weight of warm alcohol it yields a turbid solution of acid reaction. The filtered liquid, when evaporated, yields not less than 70% of the original balsam, as a brown semisolid mass which constitutes "prepared storax." This is entirely soluble in ether and carbon disulphide and almost completely soluble in benzene, but is only partially soluble in cold petroleum spirit, more freely in hot petroleum spirit, and the solution deposits crystals of cinnamic acid and styracin on cooling.

The residual pressings of the bark after obtaining the liquid storax are used under the name "*styrax calamitus*." Mixtures of storax with an inert solid are also known by the name, and formerly the resin of *Styrax officinalis* was also known in commerce under this description.

Analysis.

The British Pharmacopœia, 1914, gives the following description of *Styrax Præparatus*.

"Prepared storax is a viscid balsam obtained from the wounded trunk of Liquidambar orientalis, *Mill.*, purified by solution in alcohol, filtration and evaporation of the solvent.

Entirely soluble in alcohol (90%) and in ether. Boiled with a solution of potassium chromate and sulphuric acid it evolves an odour of benzaldehyde. Loses not more than 5% of its weight when heated in a thin layer on a water-bath for 1 hour. Acid value not less than 60 or more than 90; ester value not less than 100 or more than 146. Yields not less than 20% by weight of cinnamic acid when tested by the following process.

Dissolve 2.5 grm. of the storax in 25 c.c. of N/2 alcoholic solution of potassium hydroxide, boil for 1 hour under a reflux condenser, neutralise with N/2 solution of sulphuric acid, remove the alcohol by evaporation, and dissolve the residue in 50 c.c. of water. Shake this aqueous solution with 20 c.c. of ether; after separation remove the ethereal layer, wash it with 5 c.c. of water and add the washings to the aqueous solution, rejecting the ethereal liquid. Acidify the aqueous solution with diluted sulphuric acid and shake it with four successive portions each of 20 c.c. of ether Mix the ethereal solutions, wash with a few c.c. of water, transfer to a flask and distil off the ether. To the residue add 100 c.c. of water and boil vigorously for 15 minutes under a reflux condenser. Filter the solution while hot, cool to 15.5°, and collect on a tared filter the crystals of cinnamic acid that have separated. Repeat the extraction of the residue with the filtrate at least three times or until no more cinnamic acid is removed. Press the filter paper and crystals between blotting paper, dry in a dessicator over sulphuric acid and weigh. Add to the weight of the crystals so ascertained 0.03 grm. (representing the average amount of cinnamic acid remaining dissolved in the aqueous liquid). The total weight is not less than 0.5 grm "

The U. S. Pharmacopœia requires storax to reach the following standard:

Incinerate about 0.5 grm. of storax; not more than 1% of ash remains.

Dissolve about 10 grm. of storax, accurately weighed, in 20 c.c. of hot alcohol: the undissolved residue, after washing it on a filter with hot alcohol and drying at 100° does not exceed 2.5%. The combined filtrate and washings after evaporation of the alcohol at a temperature not exceeding 60° and drying the residue at 100° for 1 hour, leaves a brown transparent semi-liquid product representing not less than 60% of the storax taken: This product is soluble in ether with the exception of a few flakes, but only partially soluble in purified petroleum spirit.

Dissolve about 1 grm. of storax, purified as described above, and accurately weighed, in 50 c.c. of alcohol, add 0.5 c.c. of phenolphthalein solution and titrate with N/2 alcoholic potassium hydroxide solution. The acid value so obtained is not less than 56 nor more than 85.

Mix about 1 grm. of storax, purified as described, and accurately weighed, in a 250 c.c. flask with 50 c.c. of purified petroleum spirit, add 25 c.c. of N/2 alcoholic potassium hydroxide solution and allow the mixture to stand for 24 hours with frequient shaking. Then add 0.5 c.c. of phenolphthalein solution and titrate with N/2 hydrochloric acid solution.

It shows a saponification value of not less than 170 nor more than 230.

K. Dieterich recommends the following process for the analysis of liquid storax (*Pharm. Centr. Halle*, 1899, 40, 423). Water is estimated by drying 2 grm. at 100° to constant weight. The residue is ignited and the ash weighed. To determine the part soluble in alcohol, 10 grm. are weighed into a 200 c.c. beaker and dissolved in 100 c.c. of 96% alcohol by gentle warming. The liquid is filtered through a tared filter and the residue washed with 50 c.c. of hot alcohol. The filtrate and washings are collected in a tared porcelain basin and evaporated to dryness. In order to prevent creeping, it is best to float the basin on water contained in another basin which is heated on a water-bath. It is advisable to weigh with the basin a small glass rod, with which the residue is stirred in order to facilitate drying. The latter is carried out at 100° until the weight is constant. The residue on the filter, dried at 100°, gives the part insoluble in alcohol.

The direct acid value is determined by dissolving 1 grm. of the storax in 100 c.c. of 96% alcohol and titrating the solution with N/2 alcoholic potassium hydroxide, using phenolphthalein as indicator. The number of c.c. required, multiplied by 28.08, gives the direct acid number.

The procedure for the determination of the saponification number is the same as that given under Benzoin.

Storax should contain not more than 30% of water nor more than 1% of ash. The United States Pharmacopœia requires at least 60% to be soluble in alcohol and the residue to be soluble in ether and carbon disulphide. Not more than 3% should be insoluble in alcohol (the German Pharmacopœia fixes the standard at 2.5 %), the acid number should lie between 55 and 75, and the cold saponification number between 100 and 140.

The commoner adulterants of storax are turpentine rosin, castor oil, olive oil, and similar fatty oils. Ladanum resin has been found by K. Dieterich.

Samples of crude storax have been examined chiefly by continental chemists, and the following figures, compiled from their results, represent a wide scope:

	Acid value	Ester value	Saponification value
Beckurts and Brüche[1]	68–93	112–153	180–222
A. Kremel[2]	47·6	31·9	79·5
E. Dieterich	37·2–96.7	74.6–168	134.6–249
K. Dieterich[3]	57·5–59·4	....	....
Evers	52.2–56.7	173·5–184.2	230.2–236.4

[1] 6 samples of authentic origin.
[2] A sample adulterated with turpentine.
[3] 2 pure samples.

K. Dieterich has further examined a number of commercial and absolutely authentic samples, and gives the following comparative results:

	Authentic	Commercial
Water	26.21– 40.97%	19.58–31.95%
Ash	0.5 – 0.92%	0.24– 3.64%
Soluble in alcohol (after deducting water)	57.14– 65.49%	64.90– 77.17%
Acid value	59.38– 70.70	38.22– 72.29
Ester value	35.42– 74.43	47.81–110.03
Saponification value	104.67–135.36	111.89–187.76

E. Dieterich gives the following table of solubilities:

	%
90% alcohol	56.14–84.00
Acetic ether	69.40–73.60
Chloroform	69.20–72.60
Ether	65.80–82.80
Benzene	64.80–74.80
Turpentine	54.40–57.80
Carbon disulphide	62.30–67.80
Petroleum spirit	15.00–19.40

The sp. gr. should lie between 1.113 and 1.121, according to Beckurts and Brüche, who also give the amount dissolved in an equal volume of pure alcohol as 61 to 71%.

The following interesting table is given by K. Dieterich. Unfortunately, the figures for the pure storax are not given:

Pure storax with	Water, %	Ash, %	Soluble in alcohol (after deducting water), %	Acid No.	Ester No.	Saponification No.
20 % olive oil	33.73	0.62	63.87	53.65	72.98	126.63
30 % olive oil	28.22	0.47	70.59	53.08	78.34	131.42
20 % castor oil	33.96	0.51	64.72	57.21	66.84	124.05
30 % castor oil	29.30	0.33	69.66	51.31	79.88	131.19
20 % turpentine	39.56	0.61	59.30	78.40	29.53	107.93
30 % turpentine	34.62	0.53	63.36	84.40	23.01	107.05

Soluble in petroleum spirit	37.54–58.96%
Soluble in alcohol 90%	practically entirely
Soluble in ether	93.14–100%
Soluble in chloroform	almost entirely
Soluble in acetic ether	entirely
Soluble in benzene	95.75–100%
Soluble in turpentine	81.8 –99.55%
Soluble in carbon disulphide	86.8 –93.39%

Umney has proposed (*Perf. and Ess. Oil, Rec.*, 1911, **2**, 120) the following characters and tests as suitable for determining the purity and quality of the natural drug (as distinguished from that impoverished by extraction of valuable constituents with solvents).

Styrax purificatus.—The balsam obtained from the trunk of *Liquidambar orientalis*, purified by solution in alcohol and removal of the solvent.

Characters and Tests.—A brownish-yellow viscous balsam transparent in thin layers, with an agreeable odour and a balsamic taste. Entirely soluble in alcohol and ether. When heated on a water-bath for 1 hour it should not lose more than 5% in weight. When boiled with sulphuric acid and potassium dichromate it evolves an odour of oil of bitter almonds.

The acid and ester values, when determined in the usual manner, should lie between 60 and 90 and 110 and 140, respectively. To estimate the total cinnamic acid, the alcohol is evaporated from the saponified solution and the residue dissolved in 50 c.c. of water. The solution is transferred to a separator, washed with 10 c.c. of ether and the ethereal layer rejected. The aqueous liquid is acidified with N-sulphuric acid and the liberated acids extracted with ether. The ethereal solution is evaporated and the residue extracted with 100 c.c. of boiling water. The extract is filtered whilst hot, the filtrate cooled to 15° and the crystals deposited collected on a tared filter paper. The extraction of the residue is repeated twice with the filtrate heated to boiling and the crystals collected on the same filter. The latter is dried at 100° and weighed. To correct for the solubility of cinnamic acid 0.030 grm. must be added to the weight obtained. The latter should be at least 0.375 grm. from 2.5 grm. of storax.

In criticism of Umney's process, Hill and Cocking state (*Chem. and Drug.*, 1912, 52) that cinnamic acid cannot be completely extracted from the mixed organic acids by shaking three or even five times with hot water, and that it cannot be dried to constant weight at 100°. It is preferable to boil the mixed organic acids with water under a reflux condenser, and to dry the acid *in vacuo* over sulphuric acid or to dissolve it in alcohol and titrate with standard alkali.

L. van Itallie and H. J. Lemkes (*Pharm. Weekblad*, 1918, **55**, 142–149) state that it is preferable to estimate the cinnamic acid content rather than the acid or saponification value. The free cinnamic acid cannot be estimated from the acid value, which includes acids insoluble in water; moreover, if hydrolysis occurs, a high acid value results. Titration of the aqueous extract with alkali gives a much lower content of cinnamic acid than the following bromine method, which is recommended by the authors. 1 grm. of the sample is boiled with 20 c.c. of N/2 alcoholic potassium hydroxide solution for 1 hour under a reflux condenser, the mixture distilled on a water-bath and the residue dissolved in 25 c.c. of water. The solution is extracted with 20 c.c. of ether and the ethereal solution washed twice with 5 c.c. of water. The aqueous layer and the washings are diluted to about 950 c.c. treated with 10 c.c. of dilute sulphuric acid, made up to 1000 c.c. and filtered. Of the filtrate, 100 c.c. are treated with 1 grm. of potassium bromide, 10 c.c. of N/10 potassium bromate solution and 5 c.c. of sulphuric acid. After 15 minutes 1 grm. of potassium iodide is added, and then after a further 5 minutes the liberated iodine is titrated with thiosulphate. 1 c.c. of N/10 potassium bromate solution is equivalent to 0.0074 grm. of cinnamic acid.

According to Ahrens (*Z. Öffentl. Chem.*, 1912, **18**, 267) genuine *Styrax liquidus* has the following characters: the substance is mixed with sand and ground with petroleum spirit. The extract is collected, the solvent distilled off and the residue weighed. The amount soluble in petroleum spirit varies from 37.6 to 56%, average 45.2%. The acid value of the extract varies from 33.1 to 62.9, average 46.7, the cold saponification value 191.3 to 201.3, average 196.1. The iodine value of the extract should be determined if the presence of olive oil or castor oil is suspected.

Resinous Adulterants in Storax.—Ahrens and Hett (*Zeit. ang. Chem.*, 1903, **16**, 384; also *Pharm. J.*, 1904, [iv], **19**, 547) find that storax adulterated with rosin yields to petroleum spirit from 55.1 to 63.7% of extract; this has an acid value between 116.3 and 120.9, and a cold saponification value between 171.6 and 177.6. Specimens of pure storax of recent and older importation gave a petroleum spirit extract of 37.6 to 47.6% with an acid value ranging from 36.6 to 62.9 and a saponification value (cold) of 194.6 to 198.4. Adulteration with rosin is more readily detected by this method of separating and treating the petroleum spirit extract than by determining the saponification constants of the original drug, as recommended by Dieterich.

SALICYLIC ACID AND ITS ALLIES

Salicylic acid is the type of a group of compounds containing the radical hydroxyphenyl, $C_6H_4(OH)$, and has itself the constitution of a hydroxyphenyl-carboxylic acid, $C_6H_4(OH).COOH$. Thus it may be regarded as a hydroxy-benzoic acid, and as the hydroxyl and carboxyl groups occupy adjacent positions in the benzene-nucleus, salicylic acid is the *ortho-* form of the acid, all 3 modifications of which are known. The fact that 2 of the hydrogen atoms of the benzene-nucleus are replaced, renders all the compounds of the group capable of existing in ortho-, meta-, and para-modifications. In the case of the homologues of the hydroxybenzoic acids, where a third substitution of hydrogen by methyl or other alkyl-radical occurs, the number of possible isomerides is still further increased.

Isomeric Hydroxybenzoic Acids

Salicylic acid and methyl salicylate occur in many plants. *p-*Hydroxybenzoic acid has been found in the pods of *Bignonia catalpa.*

The following table exhibits the leading differences between the 3 isomeric hydroxybenzoic acids:

	Ortho-acid (salicylic acid)	Meta-acid	Para-acid
Formula	$C_6H_4<\genfrac{}{}{0pt}{}{OH(1)}{COOH(2)}$	$C_6H_4<\genfrac{}{}{0pt}{}{OH(1)}{COOH(3)}$	$C_6H_4<\genfrac{}{}{0pt}{}{OH(1)}{COOH(4)}$
Sp. gr. at 4° (Schröder)	1.4835	1.473	1.468
M p.	156.7°	200°[2]	213°–214°
Solubility:			
In water at 0°	1 in 1,100.[1]	1 in 265.	1 in 580.
In water at 15° to 18°	1 in 1,000.	1 in 108.	1 in 126.
In chloroform	Readily soluble.	Almost insoluble.	Very slightly soluble.
Reaction with ferric chloride	Deep violet colour.	No change.	Yellow flocc. ppt. sol. in excess.
Reaction when heated in a current of dry ammonia gas	Yields phenol, CO_2, etc.	Yields hydroxy-benzonitrile, $C_6H_4(OH)CN$, melting at 82°.	Yields phenol, CO_2, etc.
Products with bromine water in excess	$C_6H_2Br_3.OBr + CO_2$.	$C_6HBr_3(OBr).COOH$.	$C_6H_2Br_3.OBr + CO_2$.
Antiseptic properties	Strong.	None.	Doubtful.

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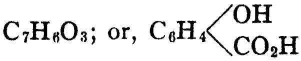
[1] According to Bourgoin (*J. Pharm. Chim.*, 1879, [iv], 30, 488), the solubility of salicylic acid at 0° is 1 part in 666, instead of the number given in the text, which is due to Ost (*J. pr. Chem.*, 1878, [ii], 17, 228).

[2] Kellas (*Zeitsch. physikal Chem.*, 1897, 24, 223) gives 188°.

SALICYLIC ACID. O-HYDROXYBENZOIC ACID



$$C_7H_6O_3;\ \text{or},\ C_6H_4\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right.$$

Salicylic acid is the only modification of the 3 isomeric hydroxybenzoic acids of any importance.

Salicylic acid and methyl salicylate occur in a number of plants and small quantities have been found in certain fruits, thus it has been detected by Jablin-Gonnet (*Ann. Chim. anal.*, 1903, **8**, 371) in wild cherries, by Suss (*Verh. Vers. deutsch Naturf. Aertze*, 1902, ii, 102), and Portes and Desmoulières (*J. Pharm. Chim.*, 1901, [vi], **14**, 342) in strawberries, and by Utz (*Oesterr. Chem. Zeit.*, 1903, **6**, 385), and Windisch (*Zeit. Nahr. Genussm.*, 1903, **6**, 447) in both strawberries and raspberries.

Salicylic acid was originally prepared from salicin (Piria, *Annalen*, 1839, **30**, 165). The so-called "natural" acid, prepared from oil of wintergreen (*Gaultheria procumbens*) or oil of sweet birch (*Betula lenta*), was first obtained by Cahours (*Annalen*, 1843, **48**, 60). Although far more expensive than the artificial product, the natural acid has the advantage of being free from *p*-hydroxybenzoic acid, which is by no means harmless in its physiological effects.

Practically the whole of the acid of commerce is now prepared by the method of Kolbe and Lautemann (*Annalen*, 1860, **115**, 157), which is based on the action of carbon dioxide on sodium phenoxide.

When potassium phenoxide is heated in a stream of carbon dioxide, it is acted on in a manner similar to sodium phenoxide in Kolbe's process, yielding pure di-potassium salicylate up to 150°; but above that temperature the isomeric *p*-hydroxybenzoate is also produced, and at 220° is the sole product.[1] The same substance is formed if the alkali employed in Kolbe's process contains potassium hydroxide, and, according to B. Fischer, it is also produced if the temperature be too low when the gas is passed. Too high a temperature is said by Fischer to cause hydroxy-*iso*phthalic acid to be formed at that stage, owing to the action of the gas on the sodium salicylate already formed. In a well-conducted operation, *p*-hydroxybenzoic and hydroxy-*iso*phthalic acids are not usually formed in quantities exceeding 0.4%, and the former may be easily removed by washing, as it is readily soluble in water. Hydroxy-*iso*phthalic acid is less soluble, and may be present to the extent of 1% in some cases.[1]

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[1] Mono-potassium salicylate is converted into the basic *p*-hydroxybenzoate and phenol when heated to 220°, whereas the corresponding sodium salt yields the *o*-hydroxybenzoate or salicylate, together with phenol.

If traces of iron compounds are present in the materials used in Kolbe's process, brown or yellow oxidation products are formed which are insoluble in water, and give a yellow colour to the salicylic acid obtained.

Salicylic acid crystallises from alcohol in large monoclinic prisms. As met with in commerce, the acid usually occurs as a granular powder, consisting of minute, broken, acicular crystals. It has a sweetish, acidulous, acrid taste. The sp. gr. is 1.483 at 4°.

The m. p. of salicylic acid has been stated by various observers at points ranging from 155° to 159°, but Fischer finds the m. p. of the pure acid to be 156.75° (corrected), and this result has been confirmed by Dunstan and Bloch (*Pharm. J. Trans.*, 1890, [iii], **21**, 429).

More recently however, it has been insisted that the true melting point is higher. H. L. Smith (*Analyst*, 1916, **41**, 3–5) found that specimens of salicylic acid prepared by different methods and dried over sulphuric acid had m. p. 158°.5 (corr:), whilst W. J. Bush & Co. (*Perf. Essent. Oil Rec.*, 1920, **11**, 207) give 159° as the melting point of pure salicylic acid and state that melting points of 158°–159° are regularly obtained with commercial samples of British salicylic acid.

Even a small proportion of the cresotic acids tends to lower the m. p. of the sample.

When gradually heated to about 200°, salicylic acid sublimes in slender shining needles, but when heated rapidly in admixture with powdered glass or sand, it is resolved into phenol and carbon dioxide. Salicylic acid distils readily in a current of steam at 60 to 80 pounds pressure, and even vaporises on boiling its aqueous solution.

Salicylic acid is very sparingly soluble in cold water, and only moderately soluble in boiling water. The determinations of its solubility by different observers vary greatly. According to the

[1] HYDROXY-*iso*PHTHALIC ACID, $C_6H_3(COOH)^1(COOH)^3(OH)^4$, is now rarely met with in commercial salicylic acid. It may be detected by distilling the suspected sample in a current of steam, when it remains in the still in the form of a light grey powder or small lumps. By dissolving it in hydrochloric acid and filtering the solution through charcoal, the acid may be obtained in slender white needles melting with decomposition at 305° to 306°.

HYDROXY-NAPHTHOIC ACID, $C_{10}H_6(OH).COOH$, is a substance which bears the same relation to naphthalene that salicylic acid bears to benzene. It is produced by the action of carbon dioxide on perfectly dry sodium α-naphthol at 130°. It forms colourless acicular crystals melting at 185° and requiring 30,000 parts of cold water for solution. Its salts give a blue coloration with ferric chloride. The corresponding acid from β-naphthol melts at 235° and gives a violet-black colour with ferric chloride. Both varieties of hydroxy-naphthoic acid are said to be powerful antiseptics, retarding the putrefaction of blood and urine much more perfectly than salicylic acid (*Pharm. J.*, 1887, [iii], **18**, 537, 823).

British Pharmacopœia (1898), the acid is soluble in about 550 parts of cold or 9 of boiling water, in 3.5 of alcohol of 90% strength, in 2 parts of ether, in 55 of chloroform, and in 195 parts of glycerin. It is also readily soluble in carbon disulphide, and is dissolved by 80 parts of benzene. Salicylic acid may be conveniently crystallised from hot petroleum spirit. Agitation with ether, chloroform, or carbon disulphide readily removes salicylic acid from its aqueous solutions. H. Taffe recommends a mixture of ether and petroleum spirit for this purpose.

The solubility of salicylic acid in cold water is greatly increased by the presence of various salts.[1]

When ingested, salicylic acid is eliminated by the kidneys, partly in an unchanged state and partly in the form of the so-called *salicyluric acid*, a compound which really has the constitution of *salicylglycocoll* $[C_6H_4(OH)CO].NH.CH_2.COOH$. This compound crystallises in fine needles, m. p., 160°, which are slightly soluble in water, but readily in alcohol. It gives a violet coloration with ferric chloride. The barium salt forms prisms very slightly soluble in water. When heated with concentrated hydrochloric acid, salicyluric acid is hydrolysed to salicylic acid and glycocoll (amino-acetic acid).

Salicylic acid and its salts and esters are used extensively in medicine, especially as intestinal antiseptics and in the treatment of gout and rheumatism of the joints.

Salicylic acid and its derivatives are now extensively employed as domestic remedies without seeking medical advice, but the practice is not free from danger. Salicylic acid, even when pure, has distinct toxic properties, and its salts cause albuminuria. The free acid, dissolved in flexible collodion or in the form of ointment, is strongly caustic and is employed as a corn solvent.

Salicylic acid now finds an extensive application as a preservative of various articles of food, though its use for such purposes is strictly prohibited in France, the United States, and some other countries.[1] Wine, beer, milk, lime- and lemon-juice, temperance beverages, and many other articles are treated with salicylic acid in quantities which are often largely in excess of those necessary to preserve them. Such a practice is strongly to be deprecated, as the habitual and unconscious ingestion of an antiseptic necessarily tends to impair the digestive processes.

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[1] Mixed with 1 part potassium nitrate, it dissolves in 50 parts of cold water.
Mixed with 1.5 parts ammonium citrate, it dissolves in 60 parts of cold water.
Mixed with 2 parts sodium sulphite, it dissolves in 50 parts of cold water.
Mixed with 2 parts sodium phosphate, it dissolves in 50 parts of cold water.
Mixed with 2.5 parts sodium phosphate, it dissolves in 12.5 parts of cold water.
Salicylic acid is very soluble in solutions of borax, a compound of the formula $Na(BO)_2C_7H_5O_3$ being said to be formed. The liquid, which is stated to be more powerfully antiseptic than either of its components, soon undergoes decomposition.

The employment of salicylic acid for preserving milk is now far less common than the use of boric acid for that purpose. Wines and temperance beverages frequently contain considerable quantities of salicylic acid,[2] and it is also used in jammaking, from 4 to 8 grains of the acid to the pound being sufficient to prevent fermentation indefinitely. Uncooked fruits, such as cherries, plums, etc., may be preserved by pressing them, treating every pound of the juice with 15 grains of salicylic acid, heating the juice, and after cooling adding it to the pressed fruit.

For a very detailed study of the influence of salicylic acid on digestion and health, see *Bull.* 84, Part II (1906), of the U. S. Dept. of Agriculture, Bur. of Chem.

The addition of 1 grm. of salicylic acid to the litre preserves a 10% solution of tartaric acid perfectly; but a solution of citric acid of the same strength requires twice that amount. Salicylic acid is stated not to have a preserving action on a solution of sodium succinate.

When an aqueous solution of salicylic acid is kept for some time, a fungoid growth forms, and this gradually decomposes all the salicylic acid (F. E. Lott, *J. Soc. Chem. Ind.*, 1903, **22**, 198). The rate of decomposition was found to be increased by the addition of small amounts of ferric chloride, thus confirming the statement that the growth of many moulds is stimulated by dilute iron solutions.

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[1] A Departmental Committee on Food Preservatives appointed in 1899 recommended that salicylic acid should not be used in greater proportion than one grain per pint in liquid food and one grain per pound in solid food, and that its presence should in all cases be declared; also that salicylic acid, in common with all other preservatives, should be prohibited in milk and in all dietetic preparations intended for invalids and infants (*Analyst*, 1901, **26**, 332). These recommendations resulted in 1906 in the issue of a circular by the Local Government Board (England) urging the desirability of prosecutions being instituted against vendors of "preserved" milk, and stating that milk may be presumed to have been rendered injurious to health if found to contain more than 1 part of formaldehyde, or 57 parts of boric acid, per 100,000 parts. A British Parliamentary Commission, appointed 1923, is now considering the question of the addition of preservatives in foods.

[2] According to medical witnesses called to defend the use of salicylic acid for this purpose, its addition is absolutely necessary to preserve the wine, and cannot possibly be injurious to health. This evidence was given at the hearing of a summons at Liverpool (October, 1900) for selling ginger wine containing 13 grains of salicylic acid to the pint. The analyst stated that of 33 samples of ginger wine examined by him, none of the others contained more than 4 grains per pint. A member of the defendant's firm deposed that they had tried smaller quantities of salicylic acid as a preservative, but found that the wine went bad.

COMMERCIAL SALICYLIC ACID

As now met with in commerce, salicylic acid, though varying much in quality, is free from those gross adulterations which are alleged to have occurred in the past.[1]

Three distinct grades of salicylic acid are now recognised in commerce, namely: ordinary acid, which is the cheapest; natural acid, which is the most expensive; and the so-called "physiologically-pure acid," which is intermediate in price. This last variety is a highly purified synthetical acid, free from any admixture of *p*-cresotic acid. Much of the ordinary salicylic acid of commerce is now of very considerable purity, and is very generally employed in medicine.

The ready formation of definite crystals is a useful indication of the purity of salicylic acid, the presence of foreign matters in its solutions greatly interfering with its crystallisation. Thus the presence of 5% of *p*-cresotic acid prevents the formation of large crystals, but 2% produces no material effect.

When agitated with cold concentrated sulphuric acid, salicylic acid should yield a perfectly colourless solution.

H. Kolbe (*J. pr. Chem.*, 1876, [ii], 14, 143) gives the following method of testing the purity of salicylic acid: 0.5 grm. of the sample is dissolved in 5 or 6 c.c. of strong alcohol, the clear solution poured on to a watch-glass, and allowed to evaporate spontaneously. The residual salicylic acid forms a ring of beautifully aggregated efflorescent crystals round the edge of the watch-glass. This mass is pure white if the acid tested be pure and recrystallised, but yellowish or yellow if the simply precipitated acid be used. If the colour be brownish or brown, the sample is unfit for internal use.

The British Pharmacopœia, 1914, gives the following standard of purity for salicylic acid:

> "Shaken with a small proportion of water, the mixture filtered and the solution evaporated, there remains a white residue, having no buff-tinted fringe (absence of iron, organic impurities, and colouring matter). When 1 grm of the acid is dissolved in excess of a cold solution of sodium carbonate, the liquid shaken with an equal volume of ether, and the ethereal solution allowed to evaporate spontaneously, the residue, if any, is free from the odour of phenol (absence of phenol). Arsenic limit, 2 parts per million. No appreciable ash."

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[1] Besides containing more or less sodium chloride, phenol, cresotic acid, and the isomerides of salicylic acid as natural impurities, salicylic acid adulterated with potassium sulphate, gypsum, starch, sugar, etc., is said to have been met with in America. Mineral adulterants would be left on igniting the sample, and starch and sugar detected by their insolubility in ether.

According to the U. S. Parmacopœia salicylic acid must have the following standard of purity.

M. p. 156°–159°

Incinerate about 1 grm. of salicylic acid; not more than 0.1% of ash remains.

Allow a saturated alcoholic solution of salicylic acid to evaporate spontaneously in a glass or porcelain dish protected from dust; the acid prepared from methyl salicylate yields a white or not more than slightly yellow or slightly pink residue (absence of iron, phenol, colouring matter).

Dissolve about 1 grm. of salicylic acid in excess of cold sodium carbonate solution, agitate the liquid with an equal volume of ether and allow the ethereal solution to evaporate spontaneously; the residue, if any, is free from odour of phenol.

A solution of about 0.5 grm. of the synthetic salicylic acid in 10 c.c. of sulphuric acid at room temperature acquires not more than a light yellow colour. The acid prepared from methyl salicylate, under similar conditions, may produce a slightly brown colour (organic impurities).

A solution of about 0.5 grm. of salicylic acid in 10 c.c. of alcohol mixed with a few drops of nitric acid, remains unaffected upon the addition of a few drops of silver nitrate solution (absence of hydrochloric acid).

Dissolve about 0.5 grm. of salicylic acid, previously dried to constant weight in a desiccator over sulphuric acid and accurately weighed, in 25 c.c. of diluted alcohol which has previously been neutralised with N/10 potassium hydroxide solution phenolphthalein being used as indicator. Titrate this solution with N/10 barium hydroxide solution, using phenolphthalein as indicator. It shows in the dried acid not less than 99.3% $C_7H_6O_3$.

Phenol is liable to be present in salicylic acid which has been sublimed. It may be detected by nearly neutralising the sample with sodium carbonate, and agitating the liquid with ether. On gently evaporating the ethereal liquid, the phenol may be recognised by its odour, taste, and chemical reactions.

It is stated by Carletti (*Boll. Chim. Farm.*, 1907, **46**, 421) that as little as 0.02% of phenol in salicylic acid can be detected in the following way: 0.25 grm. of the sample is triturated in a mortar with 5 c.c. of water and the mixture poured into a test-tube. Two drops of an alcoholic solution of furfuraldehyde (2%) are then added, the liquid gently shaken, and 2 to 3 c.c. of concentrated sulphuric acid poured carefully to the bottom of the tube. In the presence of phenol a yellow ring is formed at the junction of the 2 liquids, above which a dark blue ring subsequently appears with a rapidity depending on the amount of phenol present.

p-Hydroxybenzoic acid, which is the isomeride most likely to be present in commercial salicylic acid, may be separated by drying the acid at 60° and agitating with anhydrous chloroform. Salicylic acid dissolves readily, but *p*- and *m*-hydroxybenzoic acids remain largely undissolved.

According to H. L. Smith (*Analyst*, 1916, **41**, 3–5) a better method is based on the fact that basic calcium salicylate is less soluble than calcium *p*-hydroxybenzoate. A small quantity of the sample mixed with calcium hydroxide and water is evaporated to dryness, heated for an hour at 110° and when cold extracted with a little water. The calcium salt of the *p*-acid dissolves together with some calcium salicylate. The aqueous solution is acidified, extracted with ether and the ethereal solution filtered and evaporated to dryness. A solution of the dry residue in dry ether if allowed to evaporate on a microscope slide leaves feathery and leaf-like crystals of salicylic acid together with small dense tufts of the *p*-acid. These are readily distinguished against a dark background under a magnification of 60. If the salicylic acid contains only 1% of *p*-hydroxybenzoic acid, the crystalline tufts of the latter will predominate on the slide.

From benzoic acid, *p*-hydroxybenzoic acid may be separated by treatment with carbon disulphide, in which the latter acid is nearly insoluble.

Whilst salicylic acid is volatile in a current of steam, the isomeric hydroxybenzoic acids are not, volatile, and hence remain in the retort together with hydroxy-*iso*phthalic acid, if present. The last-named compound is now rarely met with in commercial salicylic acid. The cresotic acids behave like salicylic acid.

Commercial salicylic acid[1] formerly contained a considerable proportion of the allied acids. Thus J. Williams (*Pharm. J. Trans.*, 1877, [iii], **8**, 785) isolated from 15 to 20% of these acid impurities, but did not identify them, and Ewell and Prescott (*Pharm. J. Trans.*, 1889, [iii], **19**, 328) found still larger proportions. In 1890, Dunstan and Bloch (*Pharm. J.*, 1890, [iii], **21**, 431) further examined the specimens prepared by Williams (which had been preserved in the museum of the Pharmaceutical Society of Great Britain), and showed that they were isomeric modifications of cresotic acid, homologous with salicylic acid (see page 475).

According to M. Charteris (*Pharm. J.*, 1890, [iii], **21**, 434), it is to the presence of cresotic acid in artificial salicylic acid that the objectionable symptoms (*e. g.*, delirium, restlessness, etc.) sometimes caused by the latter are attributable, and he states that when the impurity is removed the purified product has therapeutic characters identical with those of the natural acid.[1]

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[1] Salicylic acid guaranteed to have been made from oil of wintergreen has been occasionally found to contain appreciable quantities of cresotic acid. This was in some cases due to the fact that the oil of wintergreen from which the acid had been made was nothing more than an artificial oil made in the first instance from artificial salicylic acid, the original impurities of which had been preserved during the various processes.

Formerly, commercial salicylic acid was liable to contain all 3 modifications of cresotic acid, but now a small proportion of the *p*-cresotic acid only is likely to be present.

The solubility of salicylic acid in boiling water is materially increased by the presence of cresotic acid. If, to a solution of the sample in boiling water, about 0.2 of its volume of alcohol be added and the liquid allowed to cool, pure salicylic acid will form separate, distinct, non-coherent crystals; whereas samples containing a notable proportion of cresotic acid form a network or woolly mass of small or indistinct crystals.

A very small percentage of *p*-cresotic acid materially reduces the m. p. of salicylic acid and causes it to soften at a temperature below that requisite to produce actual fusion.[2]

To detect cresotic acid in salicylic acid, B. Fischer (*Pharm. Zeit. f. Russ.*, 1889, **28**, 378) recommends the following test: Calcium carbonate (1 to 2 grm.) is boiled with 15 c.c. of water in a 200 c.c. flask, and 3 grm. of the sample of salicylic acid added. The flask is shaken over a flame till the volume of the contents is reduced to 5 c.c., by which time some crystals will have formed. The liquid is cooled, the crystals separated, and the mother liquor transferred to a test-tube and evaporated to about 1 c.c. On rubbing the tube containing this concentrated liquid with a glass rod, crystallisation sets in. 1 c.c. of water is then added and the liquid is filtered through a plug of cotton-wool. The filtrate is made up to 1 c.c. and a few drops of hydrochloric acid are added. If the sample contained as much as 3 to 5% of cresotic acid, a mixture of acids separates which fuses in boiling water and collects in thick oily drops at the bottom of the tube. This test is said to succeed only when the amount of cresotic acid exceeds 1%.

According to Engelhardt and Jones (*Amer. Pharm. Assoc. Drugg. Circ.*, 1908, **52**, 464), cresotic acids can be detected by Carletti's test (page 481) 0.20 to 0.15% of *o*-cresotic acid gives a brown colour zone, whilst with traces of phenol or *m*- or *p*-cresotic acid a faint violet colour is obtained.

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[1] In 1890, shortly after the first publication of these researches (*Brit. Med. Jour.*, Nov. 30, 1889), a prosecution under the Sale of Food and Drugs Acts was instituted in Glasgow for selling salicylic acid containing 2.5 % of cresotic acid (*Pharm. J.*, 1890, [iii], **21**, 394).

[2] "One can now obtain commercially an acid *physiologically pure*, even the last fraction of which has a m. p. of 156.85°; commercial *crystals* with a. m. p. of 156.5° to 156.75°, containing about 0.05 % impurity, the last 10 % giving a m. p. 0.5° below the maximum; commercial *powder* with an initial m. p. of 156.4°, rising to 156.75°, contaning 0.1 % impurity, the last 10 % giving a m. p. 1° below the maximum."—Squire's *Companion to the Pharmacopœia*, 1899.

The estimation of cresotic acid when in admixture with salicylic acid, if present in sufficiently large proportion, may be effected by careful titration of the sample with sodium hydroxide and phenolphthalein, as recommended by Ewell and Prescott (*Pharm. Record*, 1888; *Analyst*, 1888, **13**, 208). B. Fischer (*loc. cit.*) recommends with reason the replacement of the soda solution by decinormal baryta, which latter solution is necessarily free from carbonate. Fischer points out that the cresotic acid may be seriously overestimated, unless other impurities, such as moisture, colouring matter, and sodium chloride, be previously removed. For this purpose he recommends that the sample be dissolved in ether, and the solution filtered from any insoluble matter. The filtrate is then evaporated at a gentle heat, and the residue dried at 60°, and finally over strong sulphuric acid. When the impurity is simply water it is perhaps preferable to treat the sample with petroleum spirit, and to agitate the solution with plaster of Paris, filter and evaporate to dryness.

In carrying out the operation, about 0.2 grm. of the purified sample, weighed with the greatest possible accuracy and dried as already described at or below 60°, is treated with a few drops of an alcoholic solution of phenolphthalein, and, without adding water for solution, a centinormal solution of baryta added from a burette, with constant agitation, until the point of neutrality is approached. The flask is then rapidly warmed over a flame while the contents are kept in agitation, actual boiling being avoided until the remainder of the acid is dissolved, when the titration is completed. The baryta is preferably standardised against salicylic acid of known purity.

When pure salicylic acid is treated in the above manner, 1 grm. requires 724.4 c.c. of centinormal baryta for its neutralisation, whereas an equal weight of one of the modifications of cresotic acid will neutralise only 657.6 c.c. Hence the difference, 66.8 c.c., represents the whole distinction between the 2 acids, so that the presence of each 1% of cresotic acid will lower the volume of centinormal alkali required for 1 grm. by 0.668 c.c. Working on 0.2 grm. of the sample, this difference is reduced to 0.134 c.c. Hence extreme care in operating is essential.

Ewell and Prescott (*Pharm. Record.*, 1888; *Analyst*, 1888, **13**, 237) proposed a method of estimating cresotic acids in admixture with salicylic acid based on their conversion into the corresponding cresols on distillation with lime. They direct that 15 grm. of the sample of acid and an equal weight of lime should be thoroughly dried and well triturated, together with an equal quantity of dry iron filings, and the mixture heated strongly in a glass retort, the distillate being collected in a well-cooled receiver. The distillate is treated with just sufficient water to liquefy it, and the liquid mixed with an equal volume of 9% sodium hydroxide solution. To this solution cold water is then added gradually until precipitation commences. From the volume of water required to cause precipitation the proportion of cresotic acid present in the sample is found by the following table:

Volumes of water required to precipitate mixed soda and distillate	Percentage of cresol in distillate	Percentage of cresotic acid in sample
6.7	5	4.9
6.0	10	9.8
5·25	15	14.8
4.5	20	19.8
4·0	25	24.7
3·6	30	29.7
3·3	35	34.7
3·1	40	39·7
2.8	45	44·7
2.6	50	49·7

It is evident that such a method as the foregoing can only be roughly approximate, and is useless when the proportion of cresotic acid is very small.

In this case it is better to neutralise a fairly large quantity of the sample with calcium carbonate (mixed with boiling water) and to filter the liquid. The sparingly soluble calcium salicylate, which is deposited on cooling, is filtered off, dried, and weighed.[1] The acid remaining in solution (of which the weight is determined by difference) is precipitated with hydrochloric acid, washed, dried, and a sample analysed by one of the above methods.

Reactions and Detection of Salicylic Acid.—When salicylic acid is heated to 195° to 220° it is, according to Graebe and Eichengrün (*Annalen*, 1892, **269**, 323), to a great extent converted into phenyl salicylate, and if the product is distilled, a considerable quantity of xanthone is formed. On the other hand, if *p*-hydroxybenzoic acid is heated in an open dish to 200°, phenol and carbon dioxide are the chief products, and there finally remains only a very small quantity of some compound of high m. p. *m*-Hydroxybenzoic acid undergoes very little change even on prolonged heating at 210°.

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[1] If excess of milk of lime be substituted for calcium carbonate, a sparingly soluble basic calcium cresotate is formed, which cannot be separated from the salicylate.

Concentrated sulphuric acid dissolves pure salicylic acid without colour, forming a sulphonic acid. Impure salicylic acid gives a yellowish-brown coloration.

By the action of cold concentrated nitric acid on salicylic acid nitrosalicylic acid is formed, but with fuming nitric acid picric acid results.

Bromine gives a reaction with salicylic acid indistinguishable from that produced by phenol, and the same is true of its behaviour with Millon's reagent.

Silver nitrate and lead acetate give white precipitates with neutral salicylates, but not with free salicylic acid. Salicylic acid is not precipitated by barium or calcium chlorides, and neutral salicylates only in strong solution. Neutral salicylates in not too dilute solution (1%) give a yellowish-brown precipitate with a solution of uranium acetate. When boiled with excess of baryta water, salicylic acid is precipitated as a basic barium salt.

With a solution of cupric sulphate, salicylates and free salicylic acid give an emerald-green coloration, visible in 2,000 parts of water and destroyed by ammonia or acids.

Salicylic acid prevents the precipitation of cupric salts by alkalis, but its isomerides have not this property.

The solution of salicylic acid in 2 molecules of sodium hydroxide prevents the precipitation of ½ CuO by addition of further alkali.

Fehling's solution is reduced by salicylic acid, and under favourable circumstances may be employed for its estimation.

On heating salicylic acid or one of its salts with methyl alcohol and sulphuric acid, methyl salicylate is formed, having an agreeable aromatic odour.

Salicylic acid, by virtue of its phenolic nature, combines with formaldehyde. On dissolving the acid in a little formaldehyde solution, evaporating the liquid nearly to dryness, and then adding strong sulphuric acid a compound is precipitated which is at first practically colourless, but becomes red, whilst the solution acquires a magenta colour.

Jorissen has observed that when a solution of salicylic acid or a salicylate is treated with sodium nitrite and a little acetic acid, followed by a drop or two of copper sulphate solution, and the liquid boiled, a blood-red colour is produced, varying in intensity according to the amount of salicylic acid present. The test has been confirmed in Allen's laboratory and found very delicate. No similar reaction is produced by benzoic, cinnamic, or tartaric acid.

According to Sherman and Gross (*J Ind. Eng. Chem.*, 1911, **3**, 492), Jorissen's test, when carried out in the following manner, is considerably more delicate than that using ferric chloride. The solution to be tested is treated with 4–5 drops of a 10% solution of sodium or potassium nitrite, 4–5 drops of a 50% solution of acetic acid and 1 drop of a 1% solution of copper sulphate, the liquid being shaken after the addition of each reagent. After heating in a boiling water-bath for 45 minutes and cooling, the colour is examined against a white background, a blank test being carried out in a similar manner. In this way 0.000005 to 0.00001 grm. of salicylic acid in aqueous solution can be detected; faint but perceptible indications are obtained with 5–8 c.c. of a 1:1,000,000 solution and with 18–25 c.c. of a 1:3,500,000 solution. Benzoic, cinnamic and tartaric acids, maltol, isomaltol, orcinol, arbutin, resorcinol and phloridzin do not respond to the Jorissen test. A 1:100,000 solution of phenol gives the same colour as a 1:1,000,000 solution of salicylic acid. Saligenin gives a red colour at the dilution 1:10,000, a yellowish tint at 1:100,000, but no reaction at 1:1,000,000.

Three reactions given by Reichard (*Pharm. Zentrh.*, 1910, **51**, 743) are as follows: If a little salicylic acid be added to a small quantity of titanic acid, which has been moistened with sulphuric acid and heated for a short time, the mixture set aside for a few hours and then treated with a drop of aqueous potassium hydroxide solution, a fine orange-red coloration is produced. A mixture of salicylic acid and copper sulphate moistened with hydrochloric acid loses its green colour when exposed to the air, but after some days a reddish-violet coloration appears, resembling the biuret indication. When mixed with salicylic acid a concentrated solution of potassium ferricyanide turns dark green. This becomes bluish black on addition of a drop of strong aqueous potassium hydroxide solution, but the colour disappears on shaking, leaving the liquid a slightly green-brownish yellow.

Self has described (*Pharm. J.*, 1915, **94**, 521) a new colour test for salicylic acid. The substance to be tested is moistened with a cold mixture of equal volumes of concentrated sulphuric acid and 40% formaldehyde and then stirred with a little ammonium vanadate. For 1 mg. of salicylic acid about 2 drops of the liquid and 2–3 mg. of vanadate should be used. In the presence of salicylic acid a Prussian blue colour is produced immediately on adding the vanadate. The test is given by as little as 0.02 mg. of the acid; salicylaldehyde and methyl salicylate also respond to it. All other phenolic substances either give no coloration (except that of the reagents alone, an orange coloration changing to green) or give various shades of red, brown or green, usually changing to brown.

According to Wilkie (*J. Soc. Chem. Ind.*, 1911, **30**, 402) a perceptible precipitate of 2:4:6 tri-iodophenol is produced when equal volumes of N/10 iodine solution and N/10 sodium carbonate solution, followed after 5 minutes by excess of sulphuric acid, are added to a solution of sodium salicylate containing as little as 1 part of salicylic acid in 870,000.

McCrae states (*Analyst*, 1911, **36**, 540) that Kobert's reagent—3 drops of formaldehyde solution in 3 c.c. of sulphuric acid—gives a characteristic rose coloration with salicylic acid.

Barral describes (*Bull. Soc. Chim.* 1912 [iv], **11**, 417) four additional tests for salicylic acid. If 2 drops of a 5% solution of a salicylate are mixed in a test-tube with 2 c.c. of sulphuric acid and 10% sodium nitrite solution added, drop by drop, with continuous agitation, the liquid becomes in succession orange yellow, reddish orange, blood red with a greenish tinge, gooseberry red. On adding water it changes to orange coloured. When 2–3 c.c. of a 1% salicylic acid solution are warmed with a fragment of ammonium persulphate the size of a pea, the liquid becomes yellow, then brown and finally gives a brownish-black precipitate. On prolonged boiling the liquid becomes colourless. Three or 4 drops of a dilute salicylic acid solution dissolved in 1–2 c.c. of sulphuric acid give a stable indigo-blue colour with 2 or 3 drops of Mandelin's reagent. With salicylic acid Schlagdenhaufen's reagent in the cold gives a yellow coloration, which deepens to orange and orange brown on warming, with formation of a red precipitate of selenium and evolution of hydrogen selenide.

The first, second and fourth of these reactions are given by salicylic esters, the fourth by sulphosalicylic acid and by aspirin.

A reaction claimed to be as sensitive as that with ferric chloride has been described by P. Torti (*Boll. Chim. Farm.*, 1914, **53**, 400). When heated with a drop of nitric acid (sp. gr. 1.40) a crystal of salicylic acid dissolves, giving a yellow coloration. Even without heating a vigorous reaction commences after some time with the development of heat and liberation of nitrogen peroxide; subsequently the reaction proceeds slowly with evolution of colourless gas bubbles. After the liquid has cooled minute, shining, lemon-yellow crystals separate, which dissolve in water, alcohol or ether, forming yellow solutions. The latter give an intense red coloration with aqueous 1% ferric chloride solution.

One of the most delicate reactions for salicylic acid and soluble salicylates is that with ferric salts, which produce a beautiful violet colour even in extremely dilute solutions. The reaction is much more delicate (1 in 100,000) than that of phenol with ferric salts (1 in 3,000). The violet coloration is destroyed by alkalies with precipitation of reddish-brown ferric hydroxide. It is also destroyed by mineral acids or others capable of liberating salicylic acid.[1] Certain neutral salts, such as phosphates, tartrates, citrates, and oxalates, also interfere more or less with the reaction.

Hence before applying the test it is necessary to isolate the salicylic acid from interfering substances such as are usually present in foods and beverages. For this purpose the sample is in most cases extracted with a solvent immiscible with water, the one generally recommended being the mixture of equal volumes of ether and petroleum spirit originally proposed by Taffe. Recently, however, Taffe has advocated the use of petroleum spirit alone (*Ann. Chim. anal.*, 1903, **8**, 84; *Bull. Soc. Chim.*, 1902, [iii], **27**, 701).

A definite volume of a beverage or, in the case of a solid food, the aqueous liquid obtained by boiling the sample with sodium hydroxide solution, is acidified with phosphoric acid and then shaken with the solvent. The extract is then shaken with dilute ferric chloride solution, when the production of a violet coloration in the aqueous layer indicates the presence of salicylic acid. The test becomes more delicate if the ethereal extract, instead of being treated directly with the reagent, is shaken with dilute ammonia, the ammoniacal solution evaporated to dryness, the residue dissolved in the minimum quantity of water and the solution tested with ferric chloride.

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[1] Weiske (*J. pr. Chem.*, 1875, [ii], **12**, 157) has proposed to employ the above reaction in alkalimetry. On neutralising an acid solution to which a trace of salicylic acid and ferric chloride have been added, the violet colour becomes gradually more developed until neutrality is reached, when the liquid turns reddish-yellow. But Pagliani (*Gazzetta*, 1879, **9**, 23) has shown that the amount of mineral acid required for the destruction of the violet colour varies greatly with the nature of the acid and the dilution of the liquid, and hence salicylic acid is ill-suited for use as an indicator. This is in accord with Allen's experience.

For the extraction other solvents have been recommended. Thus Vitali (*Boll. Chim. Farm.*, 1906, **45**, 701) extracts wines with toluene. Although Gorni (*Rev. intern. Falsif.*, 1906, **19**, 16) has stated that tartaric acid is extracted from wines both by chloroform and by carbon disulphide, Dubois (*J. Amer. Chem. Soc.*, 1907, **29**, 293) advocates the use of the latter solvent as follows: The wine is extracted with ether and the ethereal solution evaporated to dryness. The residue is rubbed with 10 successive quantities (5 c.c. each) of carbon disulphide, the combined extracts evaporated, and the residue tested. The author states that carbon disulphide leaves undissolved several impurities which interfere with the colour reaction, chloroform redissolves some of the colouring matter extracted by the ether, whilst benzene, carbon tetrachloride and petroleum spirit mixed with 10% of ether, dissolve salicylic acid with difficulty.

Ferreira da Silva (*Compt. rend.*, 1900, **131**, 423), Pereira (*Bull., Soc. Chim.*, 1901, [iii], **25**, 475), Mastbaum (*Chem. Zeit.*, 1903, **27**, 829), and Spica (*Gazzetta*, 1903, **33**, ii, 482) have shown that some, but not all, natural wines known to be free from added salicylic acid, give the coloration with ferric chloride characteristic of this substance. From the observations made by Pellet (*Ann. Chim. anal.*, 1901, **6**, 328), it seems to be established that the reaction is caused by traces of salicylic acid formed naturally. For this reason it must not be concluded that a sample of wine is adulterated if a minute trace of salicylic acid is detected in it. This source of error is avoided by the German official method in which not more than 50 c.c. of the wine are used for the test.

Some liquids are preferably subjected to a preliminary treatment before extracting with a solvent. Wine, beer, or urine may be treated with lead acetate, the filtrate precipitated with a slight excess of sulphuric acid and again filtered.

For the precipitation of casein from milk Pellet recommends the use of mercuric nitrate, but Revis and Payne state that this reagent carries down a large proportion of the salicylic acid present. The method of coagulation advocated by Robin (*Ann. Chim. anal.*, 1909,

14, 53) consists in slowly adding 50 c.c. of the milk to a mixture of 10 c.c. of 5% sulphuric acid and 20 c.c. of alcohol, and filtering until a clear filtrate is obtained. The latter is extracted as described above.

Experiments made by Ferreira da Silva (*Rev. intern. Falsif.*, 1901, **14**, 68) to determine the relative sensitiveness of various methods of extracting salicylic acid from wines, show that the most delicate is the original German official method (extraction of 50 c.c. with a mixture of ether and petroleum spirit) by which 1 part in 200,000 can be detected. The modified German process (extracting the residue from the ether and petroleum spirit solution with benzene) shows 1 part in only 100,000 whilst the Weigert-Rosler method (extraction with carbon disulphide or chloroform) is equally sensitive.[1]

According to R. J. L. Schoepp (*Ned. Tydschr. Pharm.*, 1896, **7**, 67), the ferric chloride reaction is given by some specimens of beer undoubtedly free from salicylic acid, owing to the presence of *maltol*, a substance isolated by Brand from roasted malt. Sherman states (*J. Ind. Eng. Chem.*, 1910, **2**, 24) that a similar substance is present in baked cereal products and in roasted coffee. This substance, however, does not yield any characteristic reaction with Millon's reagent, with which salicylic acid gives a dark red coloration. Hence Schoepp considers it necessary in examining beer to use both tests.

In order to avoid the troublesome expedient of extracting the salicylic acid with an immiscible solvent, some authors have made use of the fact that the acid is volatile in steam. Thus Pellet (*Ann. Chim. anal.*, 1901, **6**, 364) boils 20 c.c. of the suspected liquid, acidified with phosphoric acid, and at intervals allows the escaping steam to condense on a glass rod. The liquid so condensed is added to a minute drop of ferric chloride solution, previously placed on a slightly greased porcelain plate. No reaction is obtained until the concentration of the salicylic acid in the boiling liquid has reached 0.06 to 0.07 grm. per litre, and therefore the method may be made roughly quantitative. A similar process, which is said to be particularly applicable to spirituous products, is described by von Genersich (*Zeitsch. Nahr. Genussm.*, 1908, **16**, 218–222).

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[1] C. O. Curtman (*J. Pharm. Chim.*, 1886, [v], **14**, 523) recommends the formation of methyl salicylate for the detection of salicylic acid in wine or beer. He directs that 4 c.c. of the liquid to be tested should be mixed with 2 c.c. of methyl alcohol (or failing this, ordinary alcohol), and then 2 c.c. of pure sulphuric acid cautiously added. The liquid is agitated, heated for 2 minutes, allowed to cool for 10 minutes, and then heated just to boiling, when if salicylic acid were present, a distinct odour of wintergreen oil will be perceptible. With traces, it may be necessary to allow the liquid to cool again, and then heat a third time. In examining condensed milk, etc., by this process, the sample should be digested for some hours with dilute alcohol, and the filtered liquid concentrated and heated as above.

Vitali (*Boll. Chim. Farm.*, 1906, **45**, 701) gives the following method for detecting salicylic acid in preserved tomatoes. The sample is acidified with hydrochloric acid, evaporated to a syrupy consistency, and extracted with absolute alcohol. The alcoholic extract is evaporated, the residue dissolved in a little water and the solution shaken with toluene. The toluene extract is tested for salicylic acid by shaking with dilute ferric chloride solution.

Instead of identifying the salicylic acid after extraction, by the coloration given with ferric chloride, Spica (*Gazzetta*, 1895, **25**, i, 207) has suggested the following test: The residue from the evaporation of the extract is heated with a few drops of nitric acid and excess of ammonia added. The small quantity of liquid obtained is heated with a thread of white wool, free from grease, which will be dyed bright yellow (by the picric acid formed) if salicylic acid were present. The author claims that 0.000001 grm. of salicylic acid can be recognised in this way. According to Montanari (*Gazzetta*, 1904, **34**, i, 290), the conversion into picric acid is complete only when sufficient nitric acid is used to allow the boiling to be continued for several minutes.

A number of authors have published methods of detecting salicylic acid in foods and beverages, but for the most part these only differ from those previously known in minor details, *e. g.*, in the variation of the immiscible solvent used.

Thus Stoecklin for the rapid detection in wine and beer recommends (*Ann. Falsif.*, 1912, **5**, 220) the use of dichloroethylene. This author also prefers the Jorissen test in the case of beer and bread.

von der Heide and Jakob (*Zeitsch. Nahr. Genussm.*, 1910, **19**, 137) extract wine with chloroform. For the detection in milk Philippe (*Mitt. Lebensmittel-unters. Hyg.*, 1911, **2**, 377) (see also Thomann (*Schweiz. Wochschr.*, 1912, **50**, 23)) coagulates with Fehling solution and after acidifying with hydrochloric acid, extracts with ether. Cattini (*Boll. Chim. Farm.*, 1910, **49**, 641), extracts with toluene.

Estimation. Volumetric Methods.—In the absence of other substances of acid character, free salicylic acid can be accurately estimated by titration with alkali hydroxide. Phenolphthalein is the preferable indicator, but litmus may be used. 1 c.c. of decinormal alkali solution represents 0.0138 grm. of salicylic acid. Barium hydroxide solution is preferable to potassium hydroxide or sodium hydroxide for titrating salicylic acid, as its use ensures the absence of carbonate. It is not essential that the sample should be wholly in solution before commencing the titration, but toward the end of the process any salicylic acid still remaining undissolved should be brought into solution by warming the liquid. The above method of titration is available in presence of phenol.

Salicylic acid existing in the form of metallic salicylates can also be estimated by the foregoing titration method, provided the solution be first freely acidified with dilute sulphuric acid, and the liberated salicylic acid then extracted by agitation with ether or other solvent as already described. After separating, the immiscible solvent should be shaken twice with small quantities of water to remove traces of mineral acid. The dissolved salicylic acid may then be recovered by cautious evaporation, but some loss by volatilisation is difficult to avoid. A preferable plan is to add a few drops of phenolphthalein solution, and titrate with standard baryta water, agitating between each addition. If desired, the immiscible solvent may then be separated from the neutral aqueous liquid, which may be evaporated, and the residual barium salicylate weighed or further examined.

The volatility of salicylic acid in a current of steam may be utilised for its separation from certain interfering substances, but the process is not to be recommended, as complete volatilisation is difficult to attain. The solution of the substance should be freely acidified with phosphoric acid and distilled to a low bulk, water being then added and the operation repeated several times, or until the fraction last obtained exhibits no acid reaction to phenolphthalein. Phenol, benzoic acid, and the 3 isomeric cresotic acids behave similarly to salicylic acid; but *m*- and *p*-hydroxybenzoic acids and hydroxy-*iso*-phthalic acids are not volatile with steam. When the distillation process is to be applied to wine or beer, the liquid should be rendered alkaline with sodium hydroxide, reduced to half its bulk by boiling, to drive off the alcohol, and then acidified and distilled as described above. When only traces of salicylic acid are present, the distillate should be made alkaline and concentrated before acidifying and shaking with ether or applying other tests.

Freyer (*Chem. Zeit.*, 1896, **20**, 820) devised a method of estimating salicylic acid based on the estimation of the amount of bromine which a given weight of the sample absorbs. Fresenius and Grünhut (*Zeitsch. anal. Chem.*, 1899, **38**, 292) and von Genersich (*loc. cit.*), after comparing the various methods suggested, have come to the conclusion that Freyer's process is the most accurate.

Salicylic acid is sometimes stated to be converted by treatment with bromine into dibromosalicylic acid, according to the reaction: $C_6H_4(OH).COOH + 2Br_2 = C_6H_2Br_2(OH).COOH + 2HBr$. It is probable that this equation correctly represents the action which first occurs, but numerous experiments by Allen and other observers prove that salicylic acid in aqueous solution ultimately reacts with 6 atoms of bromine (3 Br_2), to form a *tri*brominated salicylic acid,[1] this subsequently splitting up into carbon dioxide and tribromophenol, according to the equation:

$$C_7H_3Br_3O_3 = CO_2 + C_6H_3Br_3O.$$[2]

Neither this change nor the conversion of the tribromophenol into the substance $C_6H_2Br_3OBr$ by the excess of bromine affects the process, since the former reacts with 6 atoms of bromine and the latter is converted into tribromophenol on treatment with potassium iodide in acid solution:

$$C_6H_2Br_3.OBr + 2HI = C_6H_2Br_3.OH + HBr + I_2.$$

The process, as carried out in Allen's laboratory, is as follows: A known weight of the sample is dissolved in water (preferably with the aid of a little sodium hydroxide) and a volume corresponding to about 0.100 grm. of salicylic acid diluted to about 100 c.c. with water in a stoppered bottle. 10 c.c. of hydrochloric acid (sp. gr. 1.1) is next added (von Genersich states that it is preferable to add the salicylic acid solution to the bromate solution *after* the acidification of the latter), followed by a known volume (about 50 to 60 c.c.) of a solution containing sodium bromate and bromide, of which sufficient should be used to give about 75% of bromine in excess of that entering into the reaction.[1] The bottle is closely stoppered, well shaken, and allowed to remain in the dark for at least 1 hour to ensure the completion of the reaction.[2] Another bottle containing an equal quantity of the bromine solution is similarly diluted and acidified, and left to stand side by side with the sample. A solution of potassium iodide (10%) is next added to the contents of both bottles, and the liberated iodine titrated with a solution of sodium thiosulphate (24.827 grm. of $Na_2S_2O_3 + 5H_2O$ per litre). Each 1 c.c. of this thiosulphate solution required represents 0.008 grm. of bromine in excess of that which has reacted with the salicylic acid, 0.138 grm. of which causes the disappearance of 0.480 grm. of free bromine, or as much as will be liberated by about 50 c.c. of the bromine solution. The observation of the end point may be assisted by the use of starch paste, but it is important that this should not be added until the liquid is nearly decolorised. Hence, if a preparation already containing starch is to be examined, the salicylic acid must first be extracted by alcohol or other suitable solvent, and the process applied to the solution (Fresenius and Grünhut). In the case of wine and beer, the salicylic acid should be first extracted by the use of a mixture of ether and petroleum spirit, and the process applied to the aqueous liquid obtained on shaking the above solution with sodium hydroxide.

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[1] The constitution of this compound is uncertain. If it be $C_6H_2Br_2(OBr).COOH$, analogy with the substance $C_6H_2Br_3.OBr$ would lead one to expect that it would react with potassium iodide to form $C_6H_2Br_2(OH).COOH$, but this implies the combination of $2Br_2$ only, instead of $3Br_2$. On the other hand, the formation of the substance $C_6HBr_3(OH).COOH$ is not in accordance with the usual behaviour of ortho-derivatives of benzene, though it accounts for the absorption of $3Br_2$ (see E. Werner, *Bull. Soc. Chim.*, 1886, [ii], **46**, 275).

[2] Allen has further proved that the change by which the 4 atoms of bromine at first absorbed is ultimately increased to 6 occurs gradually, the reaction being accompanied by an evolution of carbon dioxide, but even after many hours the volume of gas does not approach that represented by the above equation. Determinations of the percentage of bromine show that the product obtained is a mixture (Allen and Tankard).

The bromine process of estimating salicylic acid is specially valuable in presence of benzoic acid, which is not acted on by bromine in aqueous solution. The precipitate may be filtered off, and the benzoic acid isolated from the filtrate. Cinnamic acid reacts with 4 atoms of bromine.

Telle (*J. Pharm. Chim.*, 1901, [vi], 13, 49) has proposed a somewhat similar method. This depends on the observation that when sodium hypochlorite solution is added to a solution of potassium bromide acidified with hydrochloric acid and containing salicylic acid, no bromine is liberated until the latter is completely converted into dibromosalicylic acid.

The bromometric method has been studied by I. M. Kolthoff who states that the amount of hydrochloric acid used is important (*Pharm.*

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[1] This solution is prepared by dissolving 19.5 grm. of bromine (= 6.5 c.c.) in about 100 c.c. of water containing 10 grm. of sodium hydroxide. The liquid thus obtained is boiled well, and then diluted with water to 2 litres. The solution keeps indefinitely. On addition of hydrochloric acid, the whole of the bromine present is liberated according to the equation:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$

[2] A more prolonged standing is desirable when very accurate results are required.

Weekblad, 1921, **58**, 699–702). If 25 c.c. of N/100 solution of salicylic acid are mixed with 25 c.c. of N/10 potassium bromate solution and 1 grm. of sodium bromide, and varying quantities of 4N hydrochloric acid added, allowed to stand in a stoppered flask for 5–10 minutes, treated with 5 c.c. of N/1 potassium iodide solution and titrated with N/10 thiosulphate solution, accurate results are only obtained when the amount of hydrochloric acid does not exceed 2–6 c.c. The excess of bromine has little influence on the results. With lower concentrations of salicylic acid, *e. g.* in foodstuffs, the amount of hydrochloric acid added is of lesser importance.

Messinger and Vortmann (*Ber.*, 1890, **23**, 2753) propose to precipitate salicylic acid from its alkaline solutions, by iodine, as sodium di-iodosalicylic iodide, afterwards titrating the excess of iodine with sodium thiosulphate. The reaction takes place as follows:

$$C_6H_4(OH).COONa + 3NaOH + 3I_2 = C_6H_2I_2(OI)COONa + 3NaI + 3H_2O.$$

W. Fresenius and Grünhut (*Zeit. anal. Chem.*, 1899, **38**, 292) have criticised the method adversely, but Messinger has shown that, under proper conditions, it gives accurate results (*J. pr. Chem.*, 1900, [ii], **61**, 236).[1] The process is also applicable to the estimation of phenol, thymol, and β-naphthol.

Wilkie states (*J. Soc. Chem. Ind.*, 1911, **30**, 398) that when action between a phenol (*e. g.*, salicylic acid) and iodine is allowed to proceed for 5 minutes only, the product is wholly tri-iodophenol, whilst this substance after 20 minutes is transformed into tetraiododiphenylenequinone. On this he bases the following method of estimating certain phenols. To the dilute sodium salicylate solution (the acid should be neutralised) equal volumes of N/10 iodine and N/10 sodium carbonate solution are added. After 5 minutes excess of sulphuric acid is added, and the residual iodine titrated with N/10 sodium thiosulphate solution. A pronounced fading of the brown colour due to the iodine, or in extreme cases the precipitation of 2:4:6-tri-iodophenol indicates that too little iodine has been added; in such circumstances more iodine and sodium carbonate solution should be introduced and the estimation completed in the usual manner after 5 minutes. The estimation is best effected in stoppered bottles.

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[1] F. B. Power considers the process fairly accurate. Too large an excess of alkali should not be used. He gives the following data for one of his experiments: 0.4782 grm. of bismuth salicylate was dissolved in hydrochloric acid, the bismuth precipitated by sodium hydroxide, the liquid filtered, and the filtrate made up to 250 c.c. 50 c.c. of this solution were neutralised in a stoppered bottle with sulphuric acid, and then 0.5 c.c. of a 10 % solution of sodium hydroxide added. The bottle was immersed in hot water, and when the contents were at 60°, 31 c.c. of decinormal iodine solution were added, and the flask kept warm and occasionally shaken for a few minutes. The liquid was then cooled, acidified with sulphuric acid, filtered, and the precipitate washed with a little water. The filtrate required 15.1 c.c. of thiosulphate, showing that the iodine of 15.9 c.c. had been absorbed. As 1 c.c. of decinormal iodine corresponds to 0.0023 grm. of salicylic acid, this indicated 38.25 % in the bismuth salt, against a calculated amount of 38,45 %.

The methods of Freyer and of Messinger and Vortmann are unfavourably criticised by Seidell (*J. Amer. Chem. Soc.*, 1909, **31**, 1168) who advocates the following as more satisfactory. A known weight of the sample of salicylate dissolved in a small quantity of water is introduced into a stoppered bottle and treated with 50 c.c. of strong hydrochloric acid. The solution is titrated with N/5 bromate solution, the liquid being shaken and warmed gently after each addition. The bromate solution is added until the yellow colour of free bromine persists for 5 minutes after the addition of the last two drops, the liquid having a temperature of 80° to 100°. In this reaction one molecule of salicylic acid absorbs two molecules of bromine. A variation in the method consists in treating the salicylic solution with excess of bromate, and estimating the unabsorbed bromine with standard stannous chloride solution.

The observation that a colourless solution of salicylaldehyde becomes yellow when treated with a trace of alkali, is made by R. Berg the basis of a method of estimating salicylic acid in the presence of the aldehyde (*Chem. Zeit.*, 1919, **43**, 129). To estimate salicylic acid in an ethereal solution of this substance and salicylaldehyde, the solution is extracted several times with N/20 sodium bicarbonate solution and then with water. The last aqueous extract must give a yellow colour with a drop of alkali solution; if this is not the case all the acid has not been removed, and the extraction must be repeated. The united extracts are titrated with N/20 sulphuric acid, which is added in small quantities at a time and the solution boiled to expel carbon dioxide. The final disappearance of the yellow colour denotes the end of the titration.

Gravimetric Method.—According to Bougault (*Compt. rend.*, 1908, **146**, 1403), the substance obtained by Messinger and Vortmann by the action of iodine on salicylic acid is a mixture of potassium 3:5-di-iodosalicylate with the red substance described by Lautemann (*Annalen*, 1861, **120**, 309), which was shown by Benzinger and Kammerer (*Ber.*, 1878, **11**, 557) to be tetraiododiphenylenequinone. The extreme insolubility of the latter substance furnishes a method of estimating salicylic acid, which is especially applicable in the presence of cinnamic acid. A weight of the sample containing approximately 0.1 grm. of salicylic acid is dissolved in a solution of 1 grm. of sodium carbonate in 50 c.c. of water. Excess of iodine is added, the liquid heated for 20 minutes on a water-bath, and then boiled for 10 minutes under a reflux condenser, iodine being added from time to time to ensure the presence of excess. After removing the excess of iodine with sodium sulphite, the precipitate is collected on a Gooch crucible, washed, dried, and weighed. The weight multiplied by $\frac{138}{344}$ gives the weight of salicylic acid. *p*-Hydroxybenzoic acid reacts with iodine, giving the same substance.

Autenrieth and Beuttel state (*Arch. Pharm.*, 1910, **248,** 112) that when phenol, saligenin, salicylic acid or *p*-hydroxybenzoic acid in aqueous solution is treated at ordinary temperature with excess of bromine a quantitative yield of tribromophenol bromide, $C_6H_2Br_4O$, is obtained, and the action may be used to estimate any one of these substances (in the absence of the others). A weighed quantity of the substance is dissolved in, or emulsified with, cold water and shaken thoroughly with excess of bromine-water. After standing for 6 hours or more the precipitate is collected on a weighed filter, washed with a small quantity of dilute bromine-water, dried *in vacuo* over sulphuric acid and weighed.

For the estimation of salicylic acid in wine, Bigelow treats 100 c.c. of the sample with 5 c.c. of sulphuric acid (1 :3) and extracts with 50 c.c. of carbon tetrachloride or toluene. 25 c.c. of the extract are evaporated in a tared flask and the residue weighed. The latter may afterwards be dissolved in alcohol and the solution titrated with N/100 baryta. If the proportion of acid present is less than 0.025 grm. per 100 c.c., it is more accurately estimated colorimetrically. (*U. S. Dept. Agric. Bull.*, *No.* 122, 1909, 64.)

Colorimetric Methods.—The ferric chloride reaction may be employed for the approximate colorimetric estimation of salicylic acid. When the operation is performed on the original liquid, instead of using an aqueous solution of salicylic acid as the standard of comparison, it is preferable in all cases to add a definite amount of salicylic acid to a liquid of the same kind as that in which the salicylic acid is to be estimated. Thus milk should be compared with milk, beer with beer, and urine with urine, and the standard specimen submitted to the same treatment as the sample to be compared with it. But in all cases it is preferable to extract the salicylic acid with ether before applying the iron test, as many substances weaken the colour-reaction or suppress it entirely. The ferric chloride solution should be very dilute, and must be added gradually till the coloration no longer increases. With small quantities of salicylic acid an excess of ferric chloride destroys the coloration.[1]

The following method of applying the ferric chloride reaction to the estimation of salicylic acid in organic liquids and in foods, described by S. Harvey (*Analyst*, 1903, **28**, 2), gave good results in Allen's laboratory.[2] Standard solutions of pure salicylic acid are prepared, containing, respectively, 0.100 and 0.010 grm. of the acid per 100 c.c. The salicylic acid is suspended in water and dissolved by adding a slight excess of sodium hydroxide solution, and the liquid then rendered neutral to phenolphthalein by N/10 sulphuric acid. The solutions should be freshly made when required. The use of hydrochloric acid throughout the process should be avoided, as it seems to interfere with the coloration. A 1% solution of iron-alum is used to produce the violet coloration, which is purer and more stable than that obtained with ferric chloride. The alum solution should be acidified with a few drops of dilute sulphuric acid per 100 c.c.

The liquid under examination is acidified with sulphuric acid, and extracted with a mixture of petroleum spirit and ether as already described. Syrupy and strongly alcoholic liquids should be somewhat diluted before extraction with the mixed solvents. Two successive shakings with the solvent are sufficient, and but little colouring matter is dissolved. The separated solvent is next shaken with 2 successive quantities of water containing a known amount (5 c.c.) of decinormal alkali hydroxide, the aqueous liquid being separated, carefully neutralised, and diluted to 250 c.c. or 500 c.c.[3] A known volume of this liquid is withdrawn, diluted if necessary to 100 c.c., and 1 or 2 c.c. of the iron-alum solution added. The operation is conveniently carried out in Nessler glasses, a standard being obtained in the same way by using the weaker of the 2 solutions of salicylic acid described above. The maximum amount of salicylic acid capable of being compared by this colorimetric process is 0.001 grm. per 100 c.c., but less than this amount is preferable.

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[1] According to Fajans (*Chem. Zeit.*, 1893, **17**, 69), the colorimetric estimation of salicylic acid by means of ferric chloride cannot be carried out in the presence of phenols. Advantage may be taken, however, of the fact that the latter give no colour with a solution of ferric chloride in absolute alcohol. To estimate salicylic acid, the suspected liquid is acidified and extracted with ether, the solvent being allowed to evaporate spontaneously. The residue is dissolved in 25 to 30 c.c. of absolute alcohol, introduced into a graduated tube, and mixed with a few drops of a 5 % solution of ferric chloride in absolute alcohol, until the colour ceases to darken. In a similar tube the same amount of an alcoholic solution of salicylic acid (2 in 10,000) is taken, and then a sufficiency of ferric chloride solution. Finally the darker of the two mixtures is diluted with absolute alcohol until they both show the same intensity of colour; the difference in volume is noted, and the amount of salicylic acid thus found. According to Fajans, by this process 1 part of salicylic acid in the presence of 800 parts of phenol may be accurately estimated.

[2] Pellet and de Grobert (*Bull. Assoc. chim. sucr. dist.*, 1902, **20**, 289) have described a similar method.

[3] The use of distilled water throughout the process is imperative. The accuracy of the method is impaired by the presence of more than small amounts of saline matter in the solution to be compared, and the slightest alkalinity is fatal to success. The slight acidity due to the iron-alum solution is an advantage.

For the estimation of salicylic acid in foods and beverages containing tannin, Harry and Mummery have devised a process (*Analyst*, 1905, **30**, 124) based on the fact that lead tannate is insoluble in alkalies, whilst lead salicylate is readily soluble. In the case of jam, fruit pulp, or similar substances, 50 grm. of the crushed sample are introduced into a 300 c.c. flask, together with a little water and 15 to 20 c.c. of a saturated solution of basic lead acetate. The mixture is made alkaline by the addition of 25 c.c. of approximately normal sodium hydroxide solution, and after well shaking, 15 to 20 c.c. of N-hydrochloric acid are added and the whole diluted to 300 c.c. The partial neutralisation of the alkali is required in order to obtain complete solution of the lead salicylate. After well mixing, the contents of the flask are filtered, 200 c.c. of the filtrate are acidified with hydrochloric acid, again filtered if necessary, and extracted 3 times with ether. The residue left after evaporating the combined ethereal extracts is dissolved in alcohol, the solution diluted to 100 c.c. and the salicylic acid estimated colorimetrically with ferric chloride. These authors disagree with Harvey as to the advisability of using iron-alum solution, particularly in the acid condition.

von Fellenberg adversely criticises (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 63) the process of estimating salicylic acid in jams described by Harry and Mummery, on the ground that a portion of the salicylic acid volatilises during the distillation of the ether, that the lead precipitated occludes salicylic acid, that all of the latter is not removed by three extractions with ether, and that the salicylic acid is contaminated with fruit acids which interfere with its colorimetric estimation. He modifies the process as follows: 15 grm. of the sample are mixed with 50 c.c. of warm water, the mixture neutralised with N-sodium hydroxide solution and treated with (10–*a*) c.c. of sodium citrate solution (prepared by neutralising 35 grm. of the acid with soda and diluting to 500 c.c.); *a* being the volume of

N-sodium hydroxide solution required for the neutralisation. The mixture is now treated successively with 10 c.c. of basic lead acetate solution (sp. gr. 1.24), 10 c.c. of N-sodium hydroxide solution, 5 c.c. of N-hydrochloric acid and 40 c.c. of saturated sodium chloride solution. The addition of these salts prevents salicylic acid from being retained in the lead precipitate formed. The whole mass is now diluted to 150 c.c., filtered, and 100 c.c. of the filtrate acidified with 3 c.c. of 20% hydrochloric acid and extracted with five successive quantities of 50 c.c. of ether. The combined ethereal extracts are made alkaline with 10 c.c. of N-sodium hydroxide solution, and the ether removed by distillation. The residual solution is diluted to 50 c.c., acidified with 7 c.c. of 20% hydrochloric acid and treated with a measured excess of N/50 bromine solution (prepared by dissolving 0.57 grm. of potassium bromate and 2 grm. of potassium bromide in 1 litre of water). After the lapse of 5 minutes 0.5 c.c. of 10% potassium iodide solution is added for each 10 c.c. of the bromine solution used and the liberated iodine is titrated with N/50 thiosulphate solution. Each c.c. of the latter corresponds with 0.00046 grm. of salicylic acid. The bromine and thiosulphate solutions must, in each estimation, be titrated against each other under the same conditions as to dilution, acidity, etc., as in the actual estimation. The difference in the quantities of thiosulphate solution used in the actual estimation and the blank titration gives the amount of salicylic acid present. Von Fellenberg states that the process yields only 90% of the salicyclic acid present, and that jams contain substances which combine additively with bromine, the quantity of such substances (calculated as salicylic acid) being about 0.5 grm. per 1000 grm.

In the case of milk and cream, Revis and Payne have obtained satisfactory results by the following process (*Analyst*, 1907, **32**, 286): 20 c.c. of the milk or 20 grm. of the cream are introduced into a stoppered flask and rendered exactly neutral to litmus by adding N-sodium hydroxide solution, the volume added being noted. 40 c.c. of neutral absolute alcohol are added, the flask stoppered securely, and immersed in water at 95° for 15 minutes with frequent shaking (this is essential). After cooling, a volume of water equivalent to that of the proteins and fat, less that of the alkali solution used for neutralisation, is added. For milks this correction may be taken as 2 c.c., but for creams it depends on the percentage of fat. To 20 grm. of cream containing 55% of fat 12.5 c.c. of water must be added, with 50% of fat 11.4 c.c., 40% of fat 9.3 c.c., 30% of fat 7.2 c.c., and so on. The mixture is then filtered or, better, separated by means of a centrifugal machine. 40 c.c. of the clear filtrate are introduced into a flask with 100 c.c. of water and sufficient sodium hydroxide to make the liquid distinctly alkaline, and distilled until 60 c.c. of distillate have been collected. The residue is transferred to a 250 c.c. measuring flask, treated with 2 c.c. of a potassium mercuric iodide solution, prepared by dissolving 1.35 grm. of mercuric chloride and 3.32 grm. of potassium iodide in 64 c.c. of water and adding 20 c.c. of concentrated sulphuric acid, and diluted to 250 c.c. (in the case of cream a further 1 c.c. of water is added to allow for the slight precipitation of protein). After standing for a few minutes the liquid is filtered, and 100 c.c. of the filtrate extracted 3 times with ether, using 20 c.c. at each extraction. The combined ethereal extracts, after washing with a little water, are mixed with 20 c.c. of water and 1 drop of phenolphthalein solution, and N/10 sodium hydroxide solution added until, on shaking, the lower (aqueous layer) remains red. 1 c.c. excess of the alkali is added and, after well shaking, the aqueous layer is separated. The ether is again extracted with 20 c.c. of water containing 1 c.c. of N/10 alkali, and finally with 20 c.c. of water. To the combined aqueous extracts, N/10 sulphuric acid equivalent to the alkali used, is added, the solution diluted to 100 c.c. and examined colorimetrically in the usual manner. A concentration of salicylic acid of 0.001–0.002% (not more) gives the most suitable coloration. The iron solution is best prepared by diluting a 1% ferric alum solution with 5 volumes of water and then evaporating to the original bulk. The reagent thus treated does not give a precipitate with the test solution. Boric and benzoic acids do not interfere in this method.

Dubois (*J. Amer. Chem. Soc.*, 1906, **28**, 1616) states that salicylic acid cannot be successfully separated from tinned tomatoes either by extraction with petroleum spirit or by steam distillation. He recommends the following procedure. 50 grm. of the pulped sample are introduced into a 200 c.c. flask with 50 c.c. of water, the mixture neutralised with ammonia, and 15 c.c. of milk of lime (1:10) added. The product is diluted to 200 c.c., well shaken, and filtered. 150 c.c. of the filtrate are extracted 4 times with 25 c.c. (each time) of ether, and the combined ethereal extracts washed twice with water. The ethereal solution is distilled until only 20 to 25 c.c. remain, and the residue is allowed to evaporate spontaneously. The solid residue is dissolved in hot water and the salicylic acid estimated colorimetrically.

Vierhont has described (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 664) a method of estimating salicylic acid in fruit juices, in which the substance is acidified with sulphuric acid and extracted with petroleum spirit, alcohol being added to prevent emulsification. This is stated by Heintz and Limprich (*Zeitsch. Nahr. Genussm.*, 1913, **23**, 706) to be untrustworthy, and these authors publish a very similar method but estimate the acid colorimetrically with ferric chloride. In its turn Heintz and Limprich's process has been declared untrustworthy by Serger.

van Raalte (*Chem. Weekblad*, 1912, **9**, 1004) for the estimation of salicylic acid in jams, fruit juices, etc., recommends extraction for 5 hours with dichloroethylene.

For the estimation of salicylic acid in marmalades Serger recommends (*Zeitsch. Nahr. Genussm.*, 1914, **27**, 319) the following process: 20 grm. of the substance are diluted with 30 grm. of water and heated almost to boiling. The liquid is filtered, cooled, and 25 c.c. of the filtrate introduced into a 200 c.c. separating funnel. 5 c.c. of dilute sulphuric acid (1 : 3) and 100 c.c. of a mixture of petroleum spirit (3 vols.) and chloroform (2 vols.) are added, and the mixture shaken for 3–5 minutes. After settling, 50 c.c. of the chloroform-petroleum layer are filtered into a 100 c.c. cylinder, 1 c.c. of 1% ferric chloride solution is added, and the liquid diluted with water to 100 c.c. After shaking for 1 minute the mixture is allowed to separate completely (if separation does not occur quickly 5 c.c. of ether are added and the mixture again shaken), the aqueous layer is diluted to 100 c.c., and its colour matched against that of standards prepared by treating 90 c.c. of water with 1 c.c. of 1% ferric chloride solution and measured volumes of 0.1% salicylic acid solution. The colorations compared should not be more intense than that of a N/500 potassium permanganate solution.

E. Müller-Hoessly considers (*Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 251–253) that Heintz and Limprich's and Serger's method are suitable for the rapid estimation of salicylic acid, but believes the methods proposed by von Fellenberg and Phillipe to be more trustworthy. In the latter method the use of nickel basins is recommended, and the water-cooling apparatus is replaced by an air condenser. The author points out that the +10% correction made by von Fellenberg is also necessary in Phillipe's method.

H. D. Steenbergen has described (*Chem. Weekblad*, 1917, **14**, 914–921) a method of estimating salicylic acid in foods by extracting the latter with boiling benzene in the presence of water and a little sulphuric acid. A round-bottomed flask containing 66 c.c. of benzene and a few pieces of tile is connected with an extraction apparatus containing 50 c.c. of benzene, to which an amount of the material under examination equivalent to about 0.005 grm. of salicylic acid is added together with 2 c.c. of 4N sulphuric acid, a little alcohol and just sufficient water to cause the benzene to run over. The whole is connected with a condenser and the extraction carried on for 6 hours. After cooling, a few c.c. of benzene from the extractor are shaken with water and a drop of ferric chloride solution (1 in 1000). If this gives no salicylic acid reaction, the whole of the benzene is shaken in a separating funnel with two separate 5 c.c. of N/10 potassium hydroxide solution and then washed with water. The resulting united aqueous extracts are evaporated to dryness and the residue transferred by means of 10 c.c. of N/10 hydrochloric acid and 20 c.c. of water to a long-necked stoppered flask. To this are added 1 c.c. of hydrochloric acid (sp. gr. 1.13) and 10 c.c. of a solution containing 1.67 grm. of potassium bromate and 6 grm. of potassium bromide per litre, a blank test being made at the same time. After a quarter of an hour 6 c.c. of N/2 potassium iodide solution and 1 c.c. of chloroform are added to each, and the liberated iodine titrated with N/80 thiosulphate.

To estimate salicylic acid in wine W. Fresenius and L. Grünhut (*Zeit. anal. Chem.*, 1921, **60**, 257–266) boil 500 c.c. of the sample under a reflux condenser with 50 c.c. of 2N sodium hydroxide solution for 1 hour. The mixture is then cooled, acidified with 30 c.c. of sulphuric acid (sp. gr. 1.11) and extracted twice with (200 c.c., 100 c.c.) a mixture of ether and petroleum spirit. The ethereal solution is washed three times with water and evaporated with the addition of a small quantity of water and 2 c.c. of N/1 sodium hydroxide solution. The salicylic acid in the residual aqueous solution is estimated colorimetrically. For this purpose the reagent is prepared by diluting a ferric chloride solution of sp. gr. 1.28 with 599 times its volume of water, and the standard solution by dissolving 0.4 grm. of pure salicylic acid, dried at 100°, in 5 c.c. of alcohol (96% by vol:) diluting to 1000 c.c. with water, and diluting 100 c.c. of this solution 4 litres.

An unusual method of isolating salicylic acid from wine has been described by X. Rocques (*Ann. Chim. anal.*, 1916, **21**, 117–118). Twenty c.c. of the wine are placed in a 250 c.c. conical flask, 0.5 c.c. of dilute sulphuric acid (1 : 3) are added, 15 c.c. of benzene are poured on the surface of the liquid, and the flask closed with a cork. After standing for about 18 hours, *without shaking*, the benzene layer is transferred to a test-tube and agitated with 1 c.c. of dilute ferric chloride solution. If the wine contained as little as 0.002 grm. of salicylic acid per litre, a violet coloration is obtained. The presence of tannins etc., in the wine does not interfere with the test.

For the isolation of salicylic acid from medicated drinks B. H. St. John recommends (*J. Assoc. Off. Agric. Chem.*, 1915, **1**, 343–345) extraction with a mixture of chloroform (70%) and alcohol (30%).

For the estimation of salicylic acid in urine T. W. Thoburn and P. J. Hanzlik (*J. Biol. Chem.*, 1915, **23**, 163–180) distil in steam with phosphoric acid. Blood and joint fluid they extract with ether. Similarly H. Herissey (*Compt. rend. Soc. Biol.*, 1922, **87**, 333–336) extracts blood-serum with ether in the presence of sulphuric acid. In all three cases the salicylic acid isolated is estimated colorimetrically.

According to Linke (*Apoth. Zeit.*, 1911, **26**, 1083) the coloration given by salicylic acid with ferric chloride is not, as frequently assumed, permanent. After 1 hour the violet coloration becomes reddish violet and after 12 hours brownish yellow. But if the solution is stronger than 1 in 50,000, the colour does not change for several days. Linke estimates the free salicylic acid in aspirin tablets by grinding one of these with 25 c.c. of water, adding a drop of ferric chloride solution (the *Liquor Ferri sesquichlorati* of the German Pharmacopœia diluted with 25 volumes of water) and comparing the colour produced with that of standard solutions varying in dilution from 1 in 50,000 to 1 in 200,000.

A biochemical method of estimating small quantities of salicylic acid in the presence of excess of *p*-hydroxybenzoic acid has been described by Boeseken and Waterman (*Proc. K. Akad. Wettensch. Amsterdam*, 1911, **14**, 604). These authors state that whilst *p* (and *m*-) -hydroxybenzoic acid can be used by *Penicillium glaucum* as carbon nutriment, the presence of salicylic acid in quantities of more than 1% causes a retardation in the growth of the organism. By comparing the effect on *Penicillium glaucum* of the mixture under investigation with that of standard mixtures of salicylic acid and *p*-hydroxybenzoic acid, they claim to be able to determine quantities of salicylic acid varying from 1 to 10% in an excess of *p*-hydroxybenzoic acid, with an accuracy of about 1%.

METALLIC AND ALKALOIDAL SALICYLATES

Sodium salicylate, $NaC_7H_5O_3$, H_2O forms small white crystalline plates or a crystalline powder, odourless and permanent in the air. It has a sweetish, saline and somewhat alkaline taste, and a neutral or feebly acid reaction to litmus. It is soluble in an equal weight of cold water, only slightly soluble in absolute alcohol, but soluble in 8 parts of cold rectified spirit. In boiling water and alcohol sodium salicylate is very soluble Both the alcoholic and the aqueous solutions give a violet colour with ferric chloride. On ignition, sodium salicylate evolves phenol, and leaves from 30 to 31% of Na_2CO_3. It is completely soluble in ammonia, and the solution does not reduce silver nitrate, even on boiling. Barium chloride should cause no precipitate in the aqueous solution, and the precipitate with silver nitrate should completely dissolve on addition of nitric acid and alcohol. When the solid salt is shaken in the cold with 15 parts of strong sulphuric acid, no brown coloration should be produced.

The British Pharmacopœia, 1914, states of *sodium salicylate:*

> "2 grm. heated to redness till gases cease to be evolved leave an alkaline residue which, when treated with water, filtered and well washed, yields a clear solution requiring for neutralisation not less than 24.8 c.c. of N/2 solution of sulphuric acid. When to a concentrated aqueous solution excess of diluted nitric acid is added, a precipitate is produced which collected, washed and dried responds to the tests described under Acidum Salicylicum, and the filtrate yields not more than the slightest reactions for sulphates or chlorides. Lead limit, 10 parts per million. Arsenic limit, 2 parts per million. 50 to 100 grm. kept in a closed vessel for several days do not evolve the slightest odour of phenol. Dissolves without coloration or effervescence in sulphuric acid (absence of certain organic impurities and of carbonates)."

The U. S. Pharmacopœia requires that sodium salicylate, when dried at 100°, should contain not less than 99.5% of $NaC_7H_5O_3$.

As in the case of salicylic acid, 3 qualities of sodium salicylate are recognised in commerce. Especially if not quite pure, sodium salicylate is liable to become coloured by keeping. This change is more marked when the salt is exposed to air and light. The same is true of the solution, but this may be preserved by the addition of about 1% of sodium thiosulphate.

For the analysis of sodium salicylate Alcock (*Pharm. J.*, 1906 [iv], **23**, 597) advocates the following method: 0.5 grm. of the sample and 0.5 grm. of ammonium chloride are dissolved in 10 c.c. of water, and the solution evaporated to dryness in a platinum dish. Salicylic acid, ammonia and phenol (if present) are evolved during this evaporation. The residue is gently ignited, cooled, the residual sodium chloride dissolved in water, and the solution titrated with N/10 silver nitrate solution, of which 31.2 c.c. should be required. A preliminary estimation must be made of the chloride present in the sample.

The following method of estimating salicylates has been described by Seidell (*Amer. Chem. J.*, 1912, **47**, 508). A weighed sample is placed in a 300 c.c. stoppered bottle with 1–2 c.c. of carbon tetrachloride and 100 c.c. of water. Bromine vapour is then poured into the mixture until there is a considerable excess after shaking. After half an hour 5 c.c. of carbon disulphide and 5 c.c. of 20% potassium iodide solution are added and the liberated iodine is titrated with N/10 thiosulphate solution (after adding a little more iodide no further liberation of iodine should take place). 5 c.c. of 2% potassium iodate solution are then added and the free iodine is again titrated, further additions of potassium iodide and iodate being made to ensure the completion of the action. The iodine estimated by the second titration corresponds with the hydrobromic acid formed by the action of the bromine on the salicylate, two molecules of acid being formed from one molecule of salicylate. Benzoic acid does not react with bromine under these conditions.

Lithium salicylate, $LiC_7H_5O_3$, forms a white crystalline powder, readily soluble in water and alcohol. As met with in commerce, it usually has an acid reaction. The solubility of this salt in water at 15° is about 1:0.8, and in alcohol about 1:1.7. Lithium salicylate is employed (in doses of 0.5 to 1.0 grm.) in the treatment of acute or chronic rheumatism.

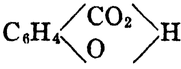
Ferric salicylate, $Fe(C_7H_5O_3)_3$, separates, on mixing a strong solution of sodium salicylate with ferric chloride, as a brown precipitate, which, together with the mother liquor, rapidly acquires a deep violet colour. After washing, ferric salicylate forms a brown amorphous substance, which yields a violet solution on boiling with water.

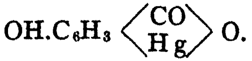
Strontium salicylate, $Sr(C_7H_5O_3)_2$, forms sparingly soluble crystals. It is highly recommended as an internal antiseptic in place of salol, and in chronic gout and rheumatism, especially when complicated by nervous disorders.

Aluminium salicylate, $Al_2(C_7H_5O_3)_6 + 3H_2O$, is obtained as a precipitate on mixing solutions of an aluminium salt and sodium salicylate. It occurs in commerce under the name of "*Salumen*" as a reddish-white, insoluble powder, which is employed as a dusting powder in catarrhal affections of the nose and pharynx.

Aluminium ammonium salicylate, $Al_2[C_6H_4(ONH_4)CO_2]_6 + 2H_2O$, is a neutral soluble salt which is more stable in solution than in the dry state. Under the name of "*Soluble Salumen*" it is used as an astringent wash for the throat and nasal passages.

Aluminium potassium salicylate has been employed as a combined astringent and antiseptic under the name "*Alkasal*" or "*Alkasol.*" Alkasal is also the name given to an aluminium potassium acetate.

Mercuric Salicylate.—A basic compound of the formula  $C_6H_4\left\langle\begin{matrix}CO_2\\O\end{matrix}\right\rangle Hg$ is obtained by mixing solutions of mercuric nitrate and sodium salicylate, and is now official in the German Pharmacopœia (Edit. iv). It forms a white amorphous powder, insoluble in water and chloroform, but soluble in a solution of sodium chloride and other haloid salts. Freshly-prepared mercuric salicylate is more soluble, and gives a stronger ferric chloride reaction than old samples. Mercuric salicylate is also somewhat soluble in ether (1:100) and in 95% alcohol (1:45). After keeping for some time the salt has an acid reaction to litmus. Mercuric salicylate keeps best in solution in sodium chloride. Mercuric salicylate is decomposed by solution of sodium carbonate.

H. Lajoux has brought forward evidence (*J. Pharm. Chim.*, 1915, [vii], **11**, 279–285) to show that this basic mercuric salicylate is best represented by the formula  $OH.C_6H_3\left\langle\begin{matrix}CO\\Hg\end{matrix}\right\rangle O$.

E. Rupp (*Arch. Pharm.*, 1901, **239**, 114) states that the method given in the German Pharmacopœia for the estimation of the mercury in mercuric salicylate (precipitation of mercuric sulphide by hydrogen sulphide) is unreliable, and recommends that 0.3 grm. of the salicylate should be rubbed down with a little water and 25 c.c. of decinormal iodine solution run in. After standing for an hour in a well-stoppered flask, the excess of iodine is estimated by titration with standard thiosulphate solution. Several estimations required 16.5 to 16.8 c.c. of decinormal iodine, practically no variation being noticed whether the action was allowed to continue for 1 hour or 15. Theoretically, 0.3 grm. of the salicylate should require 17.85 c.c. of decinormal iodine solution. The low results obtained are due to the fact that mercuric salicylate reacts with haloid salts to form a double compound, but as this is a constant, the results are quite reliable.

The following method of estimating mercury in mercuric salicylate has been described by A. Constantino (*Giorn. Farm. Chim.*, 1918, **67**, 7–12). A weighed amount (0.25 grm.) of the salt is dissolved in 2 c.c. of concentrated sulphuric acid, heated for about 6 minutes in a porcelain basin on a water-bath and diluted to 160 c.c. with water. The solution is then electrolysed for 14 minutes in a platinum dish, using a rotating platinum anode and a current of 5 volts and 6 amperes. Without stopping the current the deposit of mercury is washed with distilled water, alcohol and ether and is then dried in a desiccator. In place of the platinum dish a mercury cathode may be employed, in which case the volume of the solution should not exceed 30 c.c. and the current should be 7–10 volts and 3 amperes.

According to the U. S. Pharmacopœia, 1916, mercuric salicylate should not redden moistened blue litmus paper, should not darken *at once* on shaking about 0.1 grm. of the salt with 5 c.c. of hydrogen sulphide solution (foreign mercury compounds) and should not contain more than 0.2% of ash. The same authority gives the following method of analysis.

Digest about 0.5 grm. of mercuric salicylate, accurately weighed, in 15 c.c. of sulphuric acid and 10 c.c. of nitric acid on a water-bath until dissolved. Cool the solution, dilute with 150 c.c. of distilled water, add 30 c.c. of a solution of hydrogen dioxide and mix well. Now add gradually, with constant shaking, 5 c.c. of diluted hypophosphorous acid, then 5 grm. of sodium chloride dissolved in 20 c.c. of distilled water, stir thoroughly and allow the mixture to stand until the precipitate has subsided. Filter and wash the precipitate with distilled water. Transfer the precipitate and filter to a flask, add 50 c.c. of N/10 iodine solution and 2 grm. of potassium iodide, agitate the mixture well until all the precipitate has dissolved and titrate the excess of iodine with N/10 sodium thiosulphate solution. It shows not less than 54 nor more than 59.5% of mercury.

Bismuth salicylate, or, more correctly, *Bismuthyl salicylate* $BiO.C_7H_5O_3 + H_2O$,[1] is employed to a considerable extent in medicine. It is a white amorphous powder, insoluble in water

This salt is described by the British Pharmacopœia, 1914,[2] as follows:

> "Insoluble in water. When shaken with diluted T. Sol. of ferric chloride [5%] a violet colour is produced. Yields not more than the slightest characteristic reaction with the copper test for nitrates. Arsenic limit, 2 parts per million. When 5 grm. are shaken with 50 c.c. of ether, the ethereal solution filtered off and evaporated to dryness leaves not more than 0.005 grm. of residue (limit of free salicylic acid). Yields, when strongly heated, 62–65% of bismuth oxide. Free from silver, lead, calcium, copper, selenium, tellurium and chlorides."

The U. S. Pharmacopœia 1916 requires bismuth salicylate to give not less than 62 and not more than 66% of Bi_2O_3.

The use of alcohol as a solvent for free salicylic acid in bismuth salicylate is unsatisfactory, since it causes partial decomposition of the latter. W. Lyon (*Pharm. J.*, 1904, [iv], **18**, 219) prefers to employ 90% benzol, which is free from this objection.

Harrison (*Pharm. J.*, 1908, [iv], **27**, 349) recommends the use of ether for the same purpose.

In the examination of bismuth salicylate the estimation of the proportion of bismuth oxide left on ignition will usually be found a sufficient indication of quality, but the salicylic acid may also be separated by acidifying the solution with hydrochloric acid and agitating with ether, when the residue, left on evaporation of the ether, may be examined for *p*-cresotic acid.

Although commercial samples of bismuth salicylate may easily be obtained of a fair standard of purity, the percentage of Bi_2O_3 is very variable. From 30 to 75% of the oxide have been found by various observers.

D. B. Dott (*Pharm. J.*, 1895, [iv], **1**, 582) has described a sample of so-called bismuth salicylate which contained 47% of free salicylic acid, as estimated by treatment of the sample with ether. Bismuth

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[1] According to Martinotti and Cornelio (*Boll. Chim. farm.*, 1901, **40**, 141), commercial bismuth salicylate contains one or both of the following compounds:

$$C_6H_4(OH).COOBiO; \text{ and } C_6H_4(OH).COOBi(OH)_2.$$

P. Thibault, however (*J. Pharm. Chim.*, 1901, [vi], **14**, 22; *Bull. Soc. Chim.*, 1901, [iii], **25**, 794), has obtained a true bismuth salicylate, having the formula $Bi_2O_3.(C_7H_6O_3)_3$.

[2] It has been pointed out by several observers that no sample of bismuth salicylate, however carefully prepared, will answer to the official requirements, as the portion extracted by alcohol will invariably give a violet reaction with ferric chloride, whilst the percentage of bismuth oxide will often reach as much as 66 even in the most carefully prepared specimens. F. B. Power points out that the pharmacopœial requirements are inconsistent, since if less than 64.3 % of bismuth oxide is present there must necessarily be a corresponding excess of salicylic acid, which will give a violet coloration with ferric chloride when shaken out with alcohol.

salicylate is extensively employed for the treatment of gastric catarrh and some intestinal disorders, but the presence of more than insignificant traces of free acid renders the preparation objectionable. Samples having an exceptionally light colour generally contain a notable quantity of free acid.

Commercial bismuth salicylate is very liable to contain small quantities of bismuth *nitrate*, and, according to Green and Windridge (*Pharm. J.*, 1900, [iv], **10**, 262), this impurity is always present. For its detection, they dissolve the sample in pure sulphuric acid and add the liquid to a solution of brucine in the same acid. This latter often has a pink or rose colour, but in the presence of traces of nitrates the colour becomes a bright red which cannot be mistaken. The reaction with indigo has also been proposed for the detection of nitrate in bismuth salicylate.

For the assay of this salt Caron and Raquet have described (*Ann. Chim. anal.*, 1911, **16**, 177) the following process: 0.5 grm. of the sample is boiled for 10 minutes with 50 c.c. of N/10 sodium hydroxide and, after diluting to 100 c.c., the liquid is filtered, and 3 c.c., 10 c.c., or even 50 c.c. (according to the amount of nitrate supposed to be present) are evaporated to dryness. The residue is well mixed with 1 c.c. of pure sulphuric acid and 10 c.c. of water, and then 10 c.c. of ammonia are added. Owing to the action of the nitric acid on the salicylic acid which is also present, a nitro-derivative is formed which dissolves in ammonia with a yellow colour. The colour is then matched with that obtained from a mixture containing a known weight of sodium nitrate.

F. B. Power has found that Messinger and Vortmann's iodine process (page 496) can be satisfactorily employed for the assay of bismuth salicylate.

Bismuth cerium salicylate forms an insoluble pink powder which has proved valuable in the treatment of diseases of the gastric and intestinal mucous membranes.

Sodio-theobromine salicylate.—A compound of the formula $C_7H_7N_4O_2Na + C_6H_4(OH).COONa$, has received application in medicine under the name of "Diuretin." It is prepared by mixing aqueous solutions of molecular proportions of sodium salicylate and sodium-theobromine, and evaporating to dryness.

This compound is described in the British Pharmacopœia, 1914, as follows:

> "A white amorphous powder. No odour; taste sweetish and alkaline. Soluble in 1 part of water; soluble in alcohol; insoluble in ether and chloroform. Aqueous solution (1 in 4) alkaline to litmus and colourless; when acidified with acetic acid yields a violet coloration with T. Sol. of ferric chloride [5%], when neutralised with hydrochloric acid gives a white precipitate of theobromine, and the filtrate from this on addition of more of the acid gives a precipitate of salicylic acid; the precipitated theobromine, washed with a little water, yields, when treated with potassium chlorate and hydrochloric acid and the mixture evaporated to dryness in a porcelain dish and the residue exposed to the vapour of solution of ammonia, a purple colour. The aqueous solution also yields precipitates with T. Sol. of mercuric chloride [5%], with solutions of alkaloidal salts and with N/10 solution of iodine. Yields not less than 40% of theobromine and 35% of salicylic acid when tested by the following process: Dissolve 2 grm. of the salicylate of theobromine and sodium in 10 c.c. of warm water, slightly acidifying with diluted hydrochloric acid, add solution of ammonia until the reaction is faintly alkaline and set aside for 3 hours at 15.5°, stirring frequently. Collect the precipitated theobromine on a tared filter, wash twice with 10 c.c. of water, dry at 100° and weigh the precipitate; it weighs not less than 0.8 grm. Acidify the filtrate and washings with hydrochloric acid, shake with two successive quantities each of 10 c.c. of ether, evaporate the mixed ethereal solutions, dry the residue at 60° and weigh. It weighs not less than 0.7 grm."

According to Sztankay (*Pharm. Post.*, 1898, **31**, 189), diuretin has the composition $C_7H_8N_4O_2NaOH.OH.C_6H_4.CO_2Na$, whilst the true sodio-theobromine salicylate, $C_7H_8N_4O_2.OH.C_6H_4CO_2Na$, can be prepared by adding theobromine to warm sodium salicylate solution as long as it dissolves and then allowing to crystallise. It is less soluble in water than diuretin (*Pharm. Zeit.*, 1899, **40**, 29).

Diuretin is a white amorphous powder, freely soluble in water, but decomposed by acids. It is employed as a diuretic in cases of scarlet fever, nephritis, etc. (dose: adults 20 to 40 grains; children, 8 to 24 grains). "*Uropherin*" is the lithium compound corresponding to diuretin. It is recommended as a diuretic in doses of 15 grains.

Antipyrine salicylate is known commercially as "*Salipyrin*." It is an odourless crystalline powder melting at about 91°. It has a pleasant taste, and possesses the properties of its constituents.

Altschul states (*Pharm. Centr.-halle*, 1893, **33**, 61) that phenolphthalein is not coloured by antipyrine and that, consequently, the salicylic acid in a sample of salipyrin can be titrated with standard alkali.

Tolypyrine salicylate, commercially known as "*Tolysal*," melts at 101°, and closely resembles salipyrin.

Quinine salicylate is used to a considerable extent as an antipyretic in typhus, and as a remedy for gout and rheumatism. It forms fine white needles of the formula $C_{20}H_{24}N_2O_2, C_7H_6O_3 + H_2O$. It should contain 70% of quinine, but is very liable to be contaminated with excess of salicylic acid, for which impurity it should always be examined. Quinine salicylate dissolves in about 225 parts of cold water, in 20 parts of 90% alcohol, and in 25 parts of chloroform.

"Saloquinine," $C_6H_4(OH).COO.C_{20}H_{23}N_2O$, the quinine-ester of salicylic acid, has been recommended as an analgesic; and "*Rheumatine*," the salicylate of saloquinine, is said to be of value in rheumatic affections.

Colchicine salicylate, known in commerce as "*Colchisal*," is used, in doses of 1/100 of a grain, in the treatment of arthritis, gout, and rheumatism. It forms a yellow amorphous powder, soluble in water, alcohol, and ether. The name "colchisal" is also applied to a mixture of colchicine and methyl salicylate. The preparation is dangerous in cases of kidney disease.

SALICYLIC ESTERS

Several of the esters of salicylic acid are of considerable commercial importance, and this is specially the case with the methyl and phenyl esters.

Methyl Salicylate, $C_6H_4(OH).COO(CH_3)$.—This compound occurs naturally in the leaves of the *Wintergreen* (*Gaultheria procumbens*) and the bark of the *Sweet Birch* (*Betula lenta*), and the essential oils from these sources consist of methyl salicylate in an approximately pure condition. Methyl salicylate occurs in smaller proportion in various other plants,[1] but usually in the form of the crystallisable glucoside *gaultherin*, which under the influence of the soluble ferment *betulase* splits up into dextrose and methyl salicylate: $C_{14}H_{18}O_8 + H_2O = C_6H_{12}O_6 + C_6H_4(OH).COO(CH_3)$. The ester of wintergreen leaves and betula bark exists chiefly in the form of the glucoside, but in the former case some ready-formed methyl salicylate is also present.

In addition to the foregoing natural sources, methyl salicylate is now manufactured synthetically on a considerable scale, by distilling 2 parts of salicylic acid with 2 of methyl alcohol and 1 of strong sulphuric acid. An alternative process, which is said to give good results, is to pass dry hydrochloric acid gas through a saturated solution of salicylic acid in methyl alcohol (H. T. Thayer, *Amer. J. Pharm.*, 1895, **67**, 243; *Pharm. J.*, 1895, [iii], **25**, 1090).

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[1] The salicylic acid detected in certain fruits is probably present as methyl salicylate.

Pure methyl salicylate is a colourless or yellowish oil of peculiar aromatic odour. It has a sp. gr. of 1.1819 at 16°, and boils under the ordinary atmospheric pressure at 224°. If shaken with water and the aqueous liquid then treated with ferric chloride, a deep violet coloration is produced. When boiled with sodium hydroxide methyl salicylate is hydrolysed, with the formation of methyl alcohol and a salicylate, but with cold, dilute potassium hydroxide solution it reacts to form a crystalline compound of the formula $C_6H_4(OK).COOMe$.

Methyl salicylate is now manufactured in a state of considerable purity, and is extensively used in the treatment of rheumatism and kindred affections. It is known in commerce as "artificial wintergreen or gaultheria oil," and is said to be preferable to the natural oils of wintergreen and sweet birch, as being less liable to adulteration.[1]

According to the British Pharmacopœia, 1914, this ester should have the following properties:

> "Slightly soluble in water, readily soluble in alcohol (90%), in glacial acetic acid and in carbon disulphide. Sp. gr. 1.185 to 1.192. B. p. from 219° to 221°. Optically inactive. The solution in alcohol (90%) is neutral or faintly acid to litmus. The aqueous solution is coloured violet by the addition of a drop of T. Sol. of ferric chloride [5%]. Contains not less than 98% of the ester methyl salicylate."

Estimation.—The U. S. Pharmacopœia 1916 gives the following method of analysis for methyl salicylate:

> Introduce about 2 c.c. of methyl salicylate into a tared flask, note the exact weight, add 50 c.c. of N/2 potassium hydroxide solution, connect the flask with a reflux condenser and heat the mixture in a water-bath during 2 hours. Then add a few drops of phenolphthalein solution and titrate the excess of alkali with N/2 hydrochloric acid. It shows not less than 98% of $CH_3C_7H_5O_3$.

Gibbs (*J. Amer. Chem. Soc.*, 1908, **30**, 1465) describes the following method for estimating methyl salicylate in foods and drugs: The substance is extracted with N-sodium hydrogen carbonate solution, which dissolves the salicylic acid and a part of the ester. The remainder of the latter is isolated by acidifying with dilute sulphuric acid and distilling in steam. Both the distillate and the alkaline solution are extracted with chloroform, the chloroform extracts are boiled in a reflux apparatus with excess of potassium hydroxide, and the salicylic acid liberated is estimated.

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[1] In large quantities, methyl salicylate has marked toxic properties. A fatal case of poisoning of a middle-aged farmer who took two ounces of wintergreen oil in mistake for whisky has been recorded by B. Pillsbury (*New York Med. Record*, **58**, 150). Death occurred from exhaustion in 41 hours.

Natural gaultheria or wintergreen oil (from *Gaultheria procumbens*) contains about 99% of methyl salicylate (Power and Kleber,[1] *Pharm. Rundschau*, 1895, **13**, 228). The remaining 1% was isolated by repeatedly shaking an ethereal solution of the oil with potassium hydroxide solution, as described under birch oil (page 516). Only 1.05% of the sample was left after this treatment, and on evaporation of the ether, was obtained as a mass which was semi-solid at the ordinary temperature. Power and Kleber isolated from it the following substances: A *paraffin* m. p. 65.5° and of the probable formula $C_{30}H_{62}$; an *aldehyde* or *ketone*, which, when separated in a pure form from its hydrogen sulphite compound, had an odour like that of œnanthic aldehyde; a secondary *alcohol*, $C_8H_{16}O$, b. p. 160° to 165° corresponding to the above aldehyde or ketone; and an *ester* which on saponification yielded the above alcohol and an acid containing $C_6H_{10}O_2$, resulting by oxidation from the ketone.[2] The alcohol and ester possessed the penetrating characteristic odour which distinguishes wintergreen oil from artificial methyl salicylate, and gives the natural product its special value as a perfume.

True gaultheria oil is a colourless, yellow, or reddish liquid of a characteristic, strongly aromatic odour, which is different from that of birch oil or artificial methyl salicylate. The sp. gr. of the natural oil ranges from 1.180 to 1.187, and the b. p. from 218° to 221°. The oil is readily soluble in alcohol, ether, chloroform, and glacia lacetic acid.

True gaultheria oil (now commercially almost obsolete) differs from birch oil and artificial methyl salicylate in being feebly optically active, the value of $[a]_D$ being $-0.25°$ to $-1°$. This character is the only one besides the odour by which gaultheria oil is distinguishable from sweet birch oil, which is now very generally substituted for it.

Natural gaultheria or wintergreen oil is given a slightly different description from that of the pure ester in the British Pharmacopœia, 1914:

> "Colourless, strong characteristic odour; taste pungent. Sp. gr. 1.180 to 1.187; optical rotation at 25°, 0° to $-1°$; ref. index 1.537 to 1.539. Soluble in 6 parts of alcohol (70%) at 25°. Contains not less than 99% of esters calculated as methyl salicylate."

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[1] Cahours, in 1844, found wintergreen oil to contain 90 % of methyl salicylate and 10 % of a terpene boiling at 160°, which he called "gaultherilene." Recent analyses of gaultheria oil have failed to confirm this observation, and it is highly probable that the oil examined by Cahours was adulterated with turpentine oil.

[2] Trimble and Schröter found wintergreen and birch oils to contain traces of alcohol and benzoic acid.

Oil of sweet birch is prepared from the bark of *Betula lenta*, a tree growing extensively in some of the older places of the United States.[1] It is colourless or yellowish, but sometimes has a reddish tint from the presence of traces of iron. In odour and taste birch oil is practically indistinguishable from pure methyl salicylate, in both of which respects it differs from wintergreen oil. The optical neutrality of birch oil also distinguishes it from wintergreen oil, but the sp. gr. and b. p. are identical for the two oils.

According to Power and Kleber (*loc. cit.*), sweet birch oil is composed almost wholly of methyl salicylate, of which it contains 99.8%. To separate the small proportion of other constituents, Power and Kleber dissolve the oil in ether, and shake with a 7.5% solution of potassium hydroxide in water, when potassium methyl salicylate passes into the aqueous liquid and the other constituents are retained by the ether. By evaporation of the separated ether Power and Kleber obtained a residue from which they isolated a paraffin and ester apparently identical with those found by them in gaultheria oil; but the secondary alcohol accompanying these compounds was not found in birch oil. Both the natural and artificial varieties of methyl salicylate resemble salicylic acid in giving a deep violet coloration when their alcoholic or aqueous solutions are treated with ferric chloride.

The commercial forms of methyl salicylate, especially those of so-called natural origin, are liable to adulteration with alcohol, chloroform, sassafras oil, oil of camphor, and petroleum. The sp. gr. of the sample affords a good indication of adulteration, since all the above-named adulterants except chloroform are of less density than methyl salicylate. The solubility of the oil in 70% alcohol is also decreased by the presence of most adulterants.

If either of the forms of methyl salicylate be treated in a graduated tube with 10 volumes of a 5% aqueous solution of potassium hydroxide, it dissolves entirely, either at once or on placing the tube in boiling water, whereas any admixed oils remain undissolved, and if present in sufficient proportion can be measured. As the odour of the methyl salicylate is entirely destroyed by the treatment with alkali, the presence of chloroform and other adulterants of strong odour becomes apparent at this stage. The residual odour also distinguishes true gaultheria oil from oil of sweet birch or artificial methyl salicylate.

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[1] On the Production and Purification of Oil of Birch see the *Scientific American*, June 13, 1891: *Amer. Journ. Pharm.*, Dec., 1891; *Pharm. J.*, 1892, [iii], 22, 593.

Chloroform may also be detected by the smell when the oil is warmed. Samples containing chloroform have a high density and low b. p., whilst the density is diminished by the presence of *alcohol.* The chloroform may be approximately separated and estimated by fractional distillation, or by estimating the hydrochloric acid formed on passing the vapour mixed with hydrogen through a red-hot tube. In the portion from which the alcohol and chloroform have been separated by distillation, oil of sassafras may be recognised by its odour after addition of a hot concentrated solution of potassium hydroxide. *Sassafras oil* may also be detected by adding 3 or 4 drops of nitric acid (sp. gr. 1.3 to 1.4) to 4 or 5 drops of the oil. Sassafras oil becomes blood-red in colour, and soon changes to a brown or dark red amorphous mass. Pure methyl salicylate is unchanged at first, but after some hours it solidifies to a mass of colourless crystals, consisting of methyl nitrosalicylate.

The presence of *petroleum* greatly modifies the solubility of methyl salicylate in alcohol, besides reducing the sp. gr. *Oil of camphor* will be rectified before being used as an adulterant. If the lighter fractions be employed, these will reduce the sp. gr. of the sample and render it optically active; and the terpenes of the camphor oil can be distilled off and further examined. The heavier fractions of camphor oil contain much safrole, which can be recognised by its odour after the methyl salicylate has been saponified.

A useful control on the foregoing tests is obtained by actual estimation of the real methyl salicylate present. This may be effected by saponifying the oil with a known quantity of potassium hydroxide, and determining the excess by titration with standard acid and phenolphthalein, as in Koettstorfer's method for oils; by acidifying the liquid after saponification, extracting the liberated salicylic acid with ether, and titrating the separated ethereal solution; or by treating the sample with alkali and standard iodine, and titrating the acidified liquid with standard thiosulphate, as practised by Messinger and Vortmann. Although the oils from *Gaultheria procumbens* and *Betula lenta* contain other esters which are expressed in terms of methyl salicylate when the saponification method of assay is employed, Schimmel & Co. prefer that process to the iodine method.

Schneegans and Gerock (*Pharm. Centralb.*, 1892, **33**, 40) recommend the following as a satisfactory method of detecting free salicylic acid in such substances as artificial oil of wintergreen. One volume of the oil is shaken with 500 volumes of water, and to 100 c.c. of the liquid is added 1 c.c. of a very dilute solution of ferric chloride. If, on the addition of 5 c.c. of chloroform, the violet colour formed disappears, free salicylic acid is absent; but if it persists, the acid is present. This reaction is said to be reliable to the extent of 0.02 mg. in 1 grm. of the oil.

Gibbs (*loc. cit.*) estimates free salicylic acid in oil of gaultheria by shaking 5 to 20 c.c. with water and titrating the aqueous solution with N/50 sodium hydrogen carbonate solution, using Congo-red as indicator.

A. R. Albright has described (*J. Amer. Chem. Soc.*, 1917, **39**, 820–825) a refractometric method of detecting impurities in methyl salicylate.

Benzyl salicylate, $C_6H_4(OH).COO(C_7H_7)$, is obtained by heating benzyl chloride with a metallic salicylate to 130°–140°. It is a liquid without odour, b. p. 208°, and has been suggested as an external remedy.

Phenyl Salicylate, Salol, $C_6H_4(OH).CO.O.C_6H_5$.—This substance is now manufactured by heating the product of the action of carbon dioxide on sodium phenoxide with phosphorus oxychloride or pentachloride, when phenyl salicylate and metaphosphate and sodium chloride result. Phosgene (carbonyl chloride) may be substituted for phosphorus pentachloride (*J. Soc. Chem. Ind.*, 1886, **5**, 677).

Phenyl salicylate crystallises in rhombic prisms, m. p. 42° to 43°. It usually occurs as a white crystalline powder of very faint aromatic odour, but the dilute alcoholic solution has a smell resembling that of wintergreen oil, probably owing to the formation of traces of ethyl salicylate. It is almost tasteless, and nearly insoluble in water, but dissolves in alcohol, ether, chloroform, petroleum spirit, and liquefied carbolic acid.

The alcoholic solution of salol is coloured violet by ferric chloride, whilst bromine gives a precipitate in the form of long needles, consisting of a bromo derivative,[1] crystallising from alcohol in silky needles which melt at 98.5°. When boiled with sodium hydroxide, salol is readily saponified, and the solution, when acidified with hydrochloric acid, gives an odour of phenol and a copious precipitate of salicylic acid, which, after filtration and washing with cold water, gives with hot water a solution rendered violet by ferric chloride.

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[1] The formula of this derivative is given by some authorities as $C_{13}H_9O_3Br$, but seeing that salicylic acid and phenol are both converted by excess of bromine into the compound $C_6H_2OBr_4$, the alleged composition appears highly improbable. Tribromophenol has m. p. 96°.

Salol should not redden moistened litmus-paper; and when shaken with 50 parts of water should yield a filtrate which is not rendered violet on addition of 1 drop of ferric chloride, and does not give any immediate turbidity on adding silver nitrate or barium chloride.

Salol is employed in medicine as a substitute for metallic salicylates and wintergreen oil. Being insoluble, it passes unchanged through the stomach, but in the duodenum is decomposed into phenol and salicylic acid, and these products can be detected in the urine, which is usually very dark in colour. As an antipyretic, antiseptic, and anti-rheumatic, salol possesses properties of value. When applied externally it has no corrosive action, and its lower m. p. gives it some advantages over salicylic acid.

Salol is sometimes employed in skin and nasal diseases as a substitute for iodoform. When melted with camphor (65:84) it forms a permanent liquid, suitable for this purpose.

A 5% solution of salol in weak alcohol, flavoured in various ways, is employed for mouth-washes, dentifrices, toilet-powders, etc.

Salol is described as follows in the British Parmacopœia, 1914:

> "Alcoholic solution neutral to litmus; yields a white precipitate with solution of bromine, and a violet coloration with dilute T. Sol. of ferric chloride. When 0.2 grm. is boiled with 5 c.c. of solution of sodium hydroxide (20%) and the cooled solution acidified with hydrochloric acid, the odour of phenol is developed and a crystalline precipitate is formed. Water which has been shaken with Salol is not affected by T. Sol. of ferric chloride (absence of free salicylic acid and of readily soluble salicylates), and yields no characteristic reactions for sulphates or chlorides. No appreciable ash."

According to the U. S. Pharmacopœia, 1916, salol must be free from sulphates and chlorides, must not redden moistened blue litmus paper, and must not contain more than 0.05% of ash. When washed with water, the wash-water must give no coloration with ferric chloride solution.

Estimation.—For the estimation of salol Squire and Caines (*Pharm. J.*, 1905, [iv], **20**, 720) recommend the following process: 0.5

grm. of the sample is weighed into a flask, treated with 5 c.c. of N-sodium hydroxide solution and 10 c.c. of water, and the ester saponified by heating on a water-bath. The excess of alkali is estimated by titration with N/10 sulphuric acid. A blank experiment is made by treating 5 c.c. of the N-sodium hydroxide solution in the same way and titrating with the same acid. The difference in volume of acid required in the 2 cases is calculated into salol, 1 c.c. of N/10 acid representing 0.021408 grm. of the latter substance. The liberated phenol has no effect on the titration if phenolphthalein is used as indicator.

Telle's method (page 495) for the estimation of salicylic acid may be applied to salol after saponification with boiling aqueous sodium hydroxide. 1 molecule of salol requires 5 molecules of bromine. For the estimation in surgical dressings, the latter are extracted with alcohol (*J. Pharm. Chim.*, 1901, [vi], **14**, 289).

Beythien and Atenstadt (*Zeitsch. Nahr. Genussm.*, 1907, **14**, 392) have described a method of estimating salicylic acid, menthol, phenol, salol, and menthyl salicylate in mouth-washes, etc. This depends on the extraction of the salicylic acid with sodium hydrogen carbonate, and then the phenol with sodium hydroxide solution. The undissolved mixture of menthol, menthyl salicylate, and salol, is saponified, the total menthol separated by its insolubility in alkalies and the salicylic acid and phenol estimated in the alkaline aqueous liquid.

B. Salkover states (*Amer. J. Pharm.*, 1916, **88**, 484–485) that, whilst 100 c.c. of petroleum spirit dissolves only 0.015 grm. of phenacetin and 0.022 grm. of acetanilide, salol is readily soluble in this solvent. The author bases a method of estimating salol in the presence of the former two substances on this fact.

To estimate salol in the presence of phenacetin, W. O. Emery, G. C. Spencer and C. C. Le Febre have described (*J. Ind. Eng. Chem.*, 1915, **7**, 681–684) the following method: a quantity of the mixture containing not more than 0.1 grm. of salol is heated on a water-bath for 5 minutes with 10 c.c. of 2.5% sodium hydroxide solution, then cooled rapidly and extracted with chloroform. The chloroform solution is washed with 5 c.c. of water and the wash-water, together with the aqueous alkaline solution, is transferred to a stoppered bottle. The solution is diluted to 200 c.c. and an excess of N/7 potassium bromide-bromate solution (about 45 c.c.) is added, followed by 10 c.c. of concentrated hydrochloric acid. The mixture is shaken for 1 minute and at intervals for 30 minutes; 10 c.c. of 15% potassium iodide solution are then added, the mixture is shaken for 15 minutes and the liberated iodine titrated with N/7 sodium thiosulphate solution. Each c.c. of N/7 bromide-bromate solution is equivalent to 0.002548 grm. of salol, one molecule of which requires 6 molecules of bromine.

W. O. Emery has also described a method (*J. Ind. Eng. Chem.*, 1921, **13**, 538–539) of estimating salol, depending on the formation of a red amorphous compound di iod. phenylene oxide $C_6H_2OI_2$ when salicylic acid is treated with iodine in the presence of sodium carbonate.

A microchemical method of detecting salol has been described by G. Denigés (*Bull. Soc. pharm. Bordeaux*, 1922, **60**, 163–169).

Chlorsalol, or chlorophenyl salicylate, $C_6H_4(OH).COO(C_6H_4Cl)$, exists in 2 modifications. *o*-Chlorophenyl salicylate forms colourless crystals melting at 55° and has been used in surgery as an antiseptic. The *p*-modification melts at 72°, is insoluble in water, but soluble in alcohol, and in doses of 4 to 6 grm. daily has been used internally as a substitute for salol.

A substance analogous to salol may be obtained by substituting resorcinol for phenol. By heating a mixture of sodium salicylate and cresylate with phosphorus oxychloride, the salicylate corresponding to *o*-, *m*-, or *p*-cresol is obtained according to the modification of cresol employed. The products are termed "*Cresalols*," and have been employed as dusting powders and substitutes for salol.

Alphol and betol (or *Salinaphthol*) are the commercial names of compounds obtained by the action of sodium salicylate on α- and β-naphthol, respectively, in the presence of phosphorus oxychloride. Betol, which is the preferable isomeride, is used as an intestinal antiseptic in cases of ague and articular rheumatism. It is tasteless and odourless, with a m. p. of 95°. It is almost insoluble in water, but dissolves readily in boiling alcohol and ether.

According to Dragendorff (*Arch. Pharm.*, 1895, **233**, 612), the sulphuric acid solution of betol, when treated with a crystal of chloral hydrate, gives an orange colour which changes to reddish-violet and then to red with a green fluorescence (distinction from alphol).

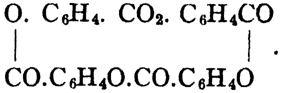
ANHYDRIDES OF SALICYLIC ACID

Salicylic Anhydride or Di-salicylic Acid,

$O[C_6H_4CO_2H]_2$,

results from the action of phosphorus oxychloride on sodium salicylate, and is also formed by the prolonged heating of salicylic acid with acetyl chloride. It is amorphous, soluble without decomposition in cold sodium carbonate solution, but converted into salicylic acid by boiling with alkali hydroxides. It gives no coloration with ferric chloride.

Salicylide; Tetrasalicylide,



$$\begin{array}{l} O.\,C_6H_4.\,CO_2.\,C_6H_4CO \\ | \qquad\qquad\qquad\qquad\quad | \\ CO.C_6H_4O.CO.C_6H_4O \end{array}.$$

This substance, m. p. 260°, is formed, together with a polymeride, m. p. 325°, when a solution of salicylic acid in xylene is treated with phosphorus oxychloride. The 2 compounds are separated by boiling chloroform, with which the salicylide forms a compound of the formula $(C_7H_4O_2)_4, 2CHCl_3$, which crystallises in fine quadratic octahedra containing 33% of loosely combined chloroform. It has been utilised for the preparation of pure chloroform (Anschütz, *Annalen*, 1893, **273**, 94). A similar compound can be obtained from *o*-cresotic acid.

Disalicylide, $(C_6H_4CO_2)_2$, has been described by Einhorn and Pfeiffer (*Ber.*, 1901, **34**, 2951).

HYDROXY-BENZALDEHYDES, $C_7H_6O_2$

***o*-Hydroxy-benzaldehyde,** $C_6H_4(OH)^1.(CHO)^2$, originally known as *salicylous* or *spiroylous acid*, is the aldehyde of salicylic acid, to which it bears the same relation as ordinary aldehyde does to acetic acid. It occurs in the essential oils of the different varieties of *Spiræa*, and likewise in the oil of *Crepis fœtida*. Salicylic aldehyde is also obtained by the oxidation of its alcohol, *saligenol*,[1] or of those glucosides which yield that substance on hydrolysis, such as salicin and populin. For the method of synthesis, see Tiemann and Reimer (*Ber.*, 1876, **9**, 824).

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[1] SALIGENOL, saligenin, or ortho-hydroxy-benzyl alcohol, $C_6H_4(OH).CH_2OH$, is described at length under "Salicin," Vol. 7, 4th Ed.

When prepared synthetically, salicylic aldehyde is usually contaminated with the corresponding *p*-aldehyde, from which, however, it is easily separated by distillation in a current of steam, in which the *o*-compound is easily volatile, whereas the *p*-substance is not.

Salicylic aldehyde is a colourless oily liquid, of pleasant aromatic odour, resembling that of oil of meadowsweet (*Spiræa ulmaria*). It has a sp. gr. of 1.1731 at 13.5°, and b. p. 196.5°. It is fairly soluble in water, easily so in alcohol and ether, and is readily extracted from its aqueous solutions by the last-named solvent. Salicylic aldehyde combines with hydrogen sulphites of the alkalis to form crystalline compounds, decomposed by dilute acids with the re-formation of the aldehyde. On oxidation salicylic aldehyde yields salicylic acid, and like the latter substance, its aqueous solutions yield a deep violet colour with ferric chloride. Like all *o*-hydroxy-aldehydes, it colours the skin a deep yellow. Its acid characters are so pronounced that it dissolves in solutions of alkali hydroxides to form crystalline compounds, and even decomposes carbonates.

Towards phenolphthalein and Poirrier's blue it reacts as a monobasic acid. In doses of 0.1 to 0.5 grm. salicylic aldehyde has been employed as an internal antiseptic and diuretic.

***p*-Hydroxy-benzaldehyde,** $C_6H_4(OH)^1.(CHO)^4$, is isomeric with salicylic aldehyde. Its methyl ether is the well-known *anise aldehyde*, or *p*-methoxy-benzaldehyde, $(CH_3O)^1.C_6H_4.(CHO)^4$, which is known in commerce as "*aubèpine*" or "artificial hawthorn." It forms the basis of many perfumes, especially of that known as "new-mown hay." It results from the oxidation of several essential oils, such as aniseed and fennel, which contain anethole, and exists therein in greater or less quantity according to the age of the oils. Anisaldehyde can also be prepared synthetically. It is an aromatic oil of sp. gr. 1.123 at 18° and b. p. 248°. On oxidation it yields *anisic acid* (page 532).

DERIVATIVES OF SALICYLIC ACID

In addition to its salts, esters, etc., already described, the derivatives of salicylic acid described in the following tables are of practical interest. Their chief applications are as antiseptics and anti-rheumatics.

DERIVATIVES OF SALICYLIC ACID

Chemical nature	Formula	Commercial name	M p., °	Solubility in			Coloration with ferric chloride	Therapeutic applications	Dose
				Water	Alcohol	Ether			
Di-iodo-salicylic acid..	$C_6H_2I_2(OH).COOH$		220 to 230	Sparingly	Readily	Readily.		Analgesic, antithermic and antiseptic.	1.5 to 4.0 grm.
Sodium di-iodo-salicylate.	$C_7H_3O_3I_2Na + 2.5H_2O$			1:50					0.5 to 1 0 grm.
Methyl di-iodo-salicylate.	$C_7H_3O_3I_2.CH_3$	Sanoform.	110		Hot, 1:10.	Sol.	.	Desiccant for wounds and ulcers. Substitute for iodoform.	External use
Di-thio-salicylic acid (No. 1 and No. 2).	$(C_7H_5O_2)_2.S_2$	......		. .	. . .	.		Substitutes for iodoform.	External use
Sodium di-thio-salicylate (No. 1).	$(C_7H_4O_2Na)_2S_2$	Dithion.		Sol.	......	..		Antiseptic, remedy for foot-and-mouth disease.	External use
Sodium di-thio-salicylate (No. 2).			......	Hygroscopic.	.. ..	... .		Antiseptic; remedy for muscular rheumatism and rheumatic fever.	0.2 to 1.0 grm
Basic bismuth di-thio-salicylate.	....	Thioform	. ..	Insol.	....	....	.... ..	In diseases of eye, ear, nose and throat; and in veterinary medicine as substitute for iodoform in treatment of eczema, erysipelas, etc.	External use.

Salicyl-sulphonic acid	$C_6H_3(SO_3H)(OH)COOH$	**Sulpho-salicylic acid**	120	Readily	Sol		Violet	In articular rheumatism valuable reagent for proteins	....
Sodium sulpho-salicylate.	$C_6H_3(SO_3Na)(OH)COOH$			Readily	Insol	Insol		Internal antiseptic substitute for salol	
o-Amino-salicylic acid	$C_7H_5O_3(NH_2)$			Cold, insol, hot, sparingly	Insol	Insol	Cherry-red colour to brown black ppt	In articular rheumatism	0 25 to 0 5 grm
Methyl-*p*-amino-*m*-hydroxy-benzoate	$C_7H_4O_3(NH_2)(CH_3)$	**Orthoform**	120	Sparingly			Brown	Antiseptic and local anæsthetic	External use and internally, 0 5 to 1 0 grm
Sodium salt of methyl-*p*-amino-*m*-hydroxy-benzo-sulphonate	$C_7H_3O_3(SO_3Na)(NH_2)(CH_3)+H_2O$	**Sulphonated orthoform**	269	Readily				Substitute for orthoform	
Methyl-*m*-amino-*p*-hydroxy-benzoate.	$C_7H_4O_3(NH_2)(CH_3)$	**New orthoform**	142	Somewhat sol			Green colour and dirty green ppt	Substitute for orthoform	

DERIVATIVES OF SALICYLIC ACID.—(*Continued*)

Chemical nature	Formula	Commercial name	M. p. °	Solubility in			Coloration with ferric chloride	Therapeutic applications	Dose
				Water	Alcohol	Ether			
Acetyl-salicylic acid	$C_6H_4(O\cdot C_2H_3O)\cdot COOH$	Aspirin	135	Insol.	Sol. (1:15)		no coloration	Anti rheumatic substitute for salicylates	
Acet-amino-ethyl salicylic acid	$C_6H_3(O\cdot C_2H_5)(NH\cdot CO\cdot CH_3)COOH$	Benzacetin	189 to 190°	Insol.				Anti neuralgic	0.5 to 1.0 grm.
Acetyl-*p*-amino-phenyl salicylate	$C_6H_4(OH)\cdot CO_2\cdot C_6H_4[NH(COCH_3)p]$	Salophen	187 to 188	Insol.	Sol.	Sol.	Violet	Substitutes for salol, in rheumatism, neuralgia and influenza	1 to 2 grm.
Acetonyl salicylate	$C_6H_4(OH)\cdot CO_2\cdot(CH_2\cdot CO\cdot CH_3)$	Salacetol, Salantol	71	Almost insol.	Cold slightly, hot readily	Hot readily			2 to 3 grm.
Condensation product of salicylic and gallic acids	$C_6H_4(OH)\cdot CO\cdot O\cdot C\cdot O\cdot C_6H_2(OH)_3$	Salitannol	210	Insol.	Sparingly	Insol.		Antiseptic substitute for salol	Chiefly external use
Condensation product of boric and salicylic acids	$B\cdot OH(O\cdot C_6H_4\cdot COOH)_2$	Borosalicylic acid						Antiseptic	External use
Mixture of boric acid and sodium salicylate		Borsalyl Borosalyl		Sol.				Antiseptic	External use
Salicylamide	$C_6H_4(OH)\cdot CO(NH_2)$		138	1:250	Sol.	Sol.		Substitute for salicylates	0.1 to 0.3 grm.
Salicyl-*a*-methyl phenylhydrazone	$C_6H_5\cdot(CH_3)N\ H\ CH(C_6H_4)OH$	Agathin, Cosmin	74	Insol.	Sol.	Sol.		Anti neuralgic and anti rheumatic	0.12 to 0.5 grm.

Salicyl-sulphonic Acid, $C_6H_3(SO_3H)(OH).COOH$.—This compound, sometimes termed sulpho-salicylic acid, is prepared by heating salicylic acid with twice its weight of sulphuric anhydride at 100°, until dissolved. On cooling and standing, brownish crystals of the sulphonic acid separate, and may be purified by crystallisation from boiling water.

Sulphosalicylic acid forms long, thin needles, m. p. 120°, which are very soluble in water. They are coloured a deep reddish-violet by ferric chloride. On fusing sulphosalicylic acid with potassium hydroxide, phenol and salicylic acid are produced, without any di-hydroxybenzene being formed.

Sulphosalicylic acid is a delicate reagent for albumin and is a useful precipitant of all varieties of proteins in urine.[1]

Sodium sulphosalicylate, $C_6H_3(OH).(COOH).SO_3Na$, is obtained by partially neutralising sulphosalicylic acid with sodium carbonate, so as to saturate the sulphonic group only. It is a readily soluble salt, which has found application as an internal antiseptic. It is stated to possess all the advantages of salol, without having the tendency of the latter to liberate free phenol in the system.

Acetyl-salicylic acid is sold commercially under the name "aspirin." It is prepared by heating salicylic acid with acetyl chloride or acetic anhydride, and recrystallising the product.

Many diverse statements have been made as to the melting point of acetylsalicylic acid, but all the authors agree that the divergences noted are due to the instability of the substance near its melting point. M. Francois (*J. Pharm. Chim.*, 1917, [vii], **15**, 213–222) gives 132°, P. N. Leech (*J. Ind. Eng. Chem.*, 1918, **10**, 288–290) 131°.5–132°.5, H. L. Dahm (*J. Ind. Eng. Chem.*, 1919, **11**, 29–30) 133°–135°, and G. Capelli (*Giorn. Chim. Ind. Appl.*, 1920, **2**, 291–300) 132°. Several of these workers point out that it is necessary to raise the temperature of the bath to 125° or 130° before introducing the capillary tube containing the acid. In 1905 the present writer made many preparations of acetylsalicylic acid which was usually purified by recrystallisation from benzene or chloroform and he regularly found that it melted *sharply* at 136°–137°

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[1] A few crystals of the reagent should be added to a small quantity of the clear urine and the liquid agitated, when a turbidity or actual precipitate will be formed if a protein be present. The precipitate produced by albumins and globulins is not affected by heat, whereas that due to albumoses and peptones dissolves, reappearing as the liquid cools. No normal or abnormal constituent of urine other than proteins is precipitated by the reagent, but these are very completely separated. 1 part of egg albumin in 20,000 of water can be detected by the test (Roch, *Pharm. Centr.*, 1889, **30**, 549).

When the pure acid is shaken with water and the liquid filtered the filtrate gives no coloration with ferric chloride, but if heated with water it is partly hydrolysed and the solution then gives the violet colour characteristic of salicylic acid.

It is used medicinally instead of salicylic acid, over which it is said to have some advantages.

This is described for the first time in the British Pharmacopœia 1914, which sets the following standard:

> "When 0.5 grm. is shaken with 20 c.c. of water and 1 drop of T. Sol. of ferric chloride [5%] is added, no violet coloration is produced (absence of salicylic acid). Lead limit, 10 parts per million. Arsenic limit, 2 parts per million. No appreciable ash."

For the estimation of salicylic acid in acetylsalicylic acid P. N. Leech (*loc. cit.*) recommends the following method. One-tenth of a grm. of the sample is placed in a dry colorimeter tube, and 1 c.c. of alcohol (excess lessens or destroys the colour when only a minute amount of salicylic acid is present) previously distilled over sodium hydroxide, is added. After the acetylsalicylic acid has dissolved 48 c.c. of water and 1 c.c. of fresh 0.1% ferric chloride solution are added. At the same time a control test is made by treating 1 c.c. of a standard salicylate solution (prepared by dissolving 0.116 grm. of dried sodium salicylate in water, adding one drop of glacial acetic acid, and diluting to 1000 c.c., each c.c. representing 0.0001 grm. of salicylic acid) in the same manner. If, within two minutes, the colour given by the acetylsalicylic acid is not more intense than that given by the standard, the proportion of free salicylic acid present does not exceed 0.1%.

H. L. Dahm likewise makes use of the ferric chloride reaction (*J. Ind. Eng. Chem.*, 1919, **11**, 29–30), but he uses as standard a series of solutions of cobalt chloride.

The following method of estimating free acetic acid in acetylsalicylic acid has been described by A. N. Smith (*Pharm. J.*, 1920, **105**, 90–94). 1 grm. of the sample is spread in a thin layer on the surface of a piece of "robe-muslin" tied over the top of a funnel 3.5 in. in diameter; the stem of the funnel fits through a hole in a ground glass plate and the whole is covered with a bell-jar 4 in. in diameter. A tube from the top of the bell-jar is connected with a vessel containing water (previously boiled) and this in turn with a water-pump by means of which a current of pure air is aspirated through the apparatus. The air enters through the stem of the funnel, passes through the layer of acetylsalicylic acid and then bubbles through the water; the acetic acid is absorbed and is estimated by titration with N/500 sodium hydroxide solution. Free salicylic acid does not volatilise under these conditions. The acetylsalicylic acid should be covered with a second piece of muslin and each piece held to the funnel by a rubber band. Air should be aspirated for 1 hour.

Estimation.—Acetyl-salicylic acid reacts towards cold potassium hydroxide solution as a monobasic acid, when phenolphthalein is used as indicator. Since 1 grm. requires 55.54 c.c. of N/10 alkali, whilst the same weight of salicylic acid requires 72.44 c.c., every 1% of the latter acid, present as impurity, raises the volume of alkali required to neutralise 1 grm. 0.169 c.c. above the former figure (55.54). If the neutralised liquid is boiled for a few minutes with excess of the N/10 alkali, an equal volume to that used for neutralisation will be absorbed if the substance is pure, whilst, if salicylic acid is present, a smaller volume will be required.

The titration is best effected as follows: 1 grm. of the sample is weighed into a 200 c.c. flask, dissolved in a small quantity of alcohol, a drop of phenolphthalein solution added, and the liquid titrated as quickly as possible with N/10 potassium hydroxide solution, the volume required being noted. To the liquid a volume of N/10 alkali, about 5 c.c. in excess of that already used, is added, the solution boiled for 5 minutes, and the excess of alkali titrated with N/10 acid. The total volume of N/10 alkali required will be double that used in the cold neutralisation if the sample is free from salicylic or any other acid. If the sole impurity is salicylic acid, every 1% present will depress the total volume of alkali absorbed by 1 grm., 0.38 c.c. below 111.08 c.c., the volume required by the pure acid. 1 c.c. of cold N/10 potassium hydroxide solution neutralises 0.0180064 grm., whilst the same volume of the boiling alkali reacts with 0.0090032 grm. of acetylsalicylic acid.

Since cold potassium hydroxide solution slowly hydrolyses acetylsalicylic acid, the cold titration must be effected quickly, or erroneous results will be obtained.

The same method has been described by François (*loc. cit.*) and by Astruc (*J. Pharm. Chim.*, 1913, [vii], **8**, 5).

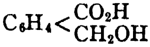
For the estimation of acetylsalicylic acid and sodium salicylate in mixtures R. Miller (*Amer. J. Pharm.*, 1917, **89**, 347–348) extracts with ether and estimates the sodium salicylate in the residue.

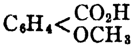
Phenyl acetylsalicylate, obtained by acetylating salol has been introduced commercially under the name "vesipyrin" (Zernik, *Apoth. Zeit.*, 1907, **22**, 152). It is a white, almost tasteless powder, m. p. 97°, insoluble in water, but readily soluble in alcohol and ether. The alcoholic solution gives no coloration with ferric chloride. It is easily saponified with boiling aqueous alkalies.

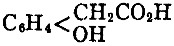
HOMOLOGUES OF SALICYLIC ACID

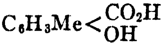
A large number of acids are known of the empirical formula $C_8H_8O_3$. Thus:

(A.) Phenyl-glycollic acids. Mandelic acid.... $C_6H_5.CH<^{CO_2H}_{OH}$

(B.) Hydroxy-methyl-benzoic acids...........  $C_6H_4<^{CO_2H}_{CH_2OH}$

(C.) Methoxy-benzoic acids (*e.g.*, anisic acid)..  $C_6H_4<^{CO_2H}_{OCH_3}$

(D.) Hydroxy-phenylacetic acids.............  $C_6H_4<^{CH_2CO_2H}_{OH}$

(E.) Hydroxy-toluic acids (*e. g.*, cresotic acids)  $C_6H_3Me<^{CO_2H}_{OH}$

Ten chemical modifications of hydroxy-toluic acid exist, and 3 each (ortho-, meta-, and para-) of hydroxy-phenylacetic, methoxy-benzoic, and hydroxy-methylbenzoic acids are known. The hydroxy-phenylacetic acids are analogues of hydracrylic acid, whilst mandelic acid corresponds to ordinary lactic acid.

The hydroxy-methylbenzoic acids are alcohols, whereas the hydroxy-phenylacetic and hydroxytoluic acids have a phenolic constitution.

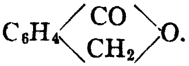
Mandelic acid, $C_6H_5.CH(OH).COOH$, contains an asymmetric carbon atom, and hence, like lactic acid, occurs in 3 sterio-isomeric forms, 2 of which exhibit optical activity in opposite directions ($[a]_D = 158°$ at 20°), whilst the third or racemic variety is obtainable by mixing the 2 optically active isomerides in equal proportions.

Inactive mandelic acid crystallises in orthorhombic prisms, m. p. 118°, readily soluble (16:100) in cold water, alcohol, and ether. On oxidation by nitric acid, mandelic acid first yields *benzoylformic acid* and ultimately *benzoic acid.*

The optically-active mandelic acids behave like the inactive acid with reagents, but melt at 133°. The lævo-rotatory modification occurs naturally, and may be obtained by digesting amygdalin with fuming hydrochloric acid for some hours at 100°. Fermentation of the ammonium salt of the inactive acid with *Penicillium glaucum* destroys the lævo-acid and leaves the dextro-modification; whereas *Schizomycetes* destroy the dextro-acid and leave the lævo-rotatory modification. The 2 active modifications can be prepared from the inactive acid by converting it into a cinchonine salt and adding a crystal of cinchonine dextro-mandelate, when the salt of the dextro-acid crystallises out, leaving that of the lævo-acid in solution.

Hydroxymethyl-benzoic Acids, $C_6H_4(CH_2OH).COOH$.—The ortho-modification melts at 120° (with simultaneous conversion into the anhydride, "phthalide"), the meta- at 180°, and the para-acid at 181°.

***o*-Hydroxymethyl-benzoic acid** is obtained by the action of alkalies on its anhydride, *phthalide.* On acidifying the solution the acid is precipitated as a powder slightly soluble in cold water but readily in alcohol. When heated to its m. p., the acid is converted into its anhydride, which is also formed by simply boiling the acid with water.

***o*-Hydroxymethyl-benzoic Anhydride,** or *Phthalide*,  $C_6H_4\left\langle\begin{matrix}CO\\CH_2\end{matrix}\right\rangle O$.

This compound is formed as stated above, and may be obtained by a variety of synthetic reactions (Wislicenus, *Ber.*, 1884, **17**, 2181). It crystallises from boiling water in needles which have an odour like that of cinnamon. Phthalide has m. p. 73° and b. p. 290°. It does not combine with hydrogen sulphites nor reduce ammonio-silver nitrate, and it yields no compound with hydroxylamine. Phthalide is oxidised to phthalic acid by treatment with alkaline permanganate. It is reduced to *o*-toluic acid by heating with hydriodic acid and phosphorus, and yields *o*-toluic acid and a little *o*-xylene when heated with zinc dust.

Methoxybenzoic Acids, $C_6H_4(OCH_3).COOH$.—The 3 modifications of this compound have the following characters:

	COOH: OCH_3	M. p., °	B. p., °	Crystalline form
Ortho-acid. Methyl-salicylic acid.	1 : 2	98.5°	....	Monoclinic tablets and prisms.
Meta-acid...... . .	1 : 3	107°	....	White needles.
Para-acid. Anisic acid.	1 : 4	184°	275°–280°	Monoclinic prisms or needles.

o-**Methoxybenzoic acid or methyl-salicylic acid** is isomeric with methyl salicylate. It crystallises from hot water in large monoclinic tablets, and from alcohol in prisms, m. p. 98.5°, and decomposing above 200° into *anisole*, $C_6H_4.OCH_3$, and carbon dioxide. When heated with concentrated hydrochloric or hydriodic acid, methyl-salicylic acid yields salicylic acid and methyl chloride or iodide.

Methyl-salicylic acid gives no violet coloration with ferric chloride.

Anisic acid, $C_6H_4(OCH_3).COOH$, has the constitution of *p-methoxy-benzoic acid.* It was first obtained in 1839 by the oxidation of anise oil, and subsequently by similar treatment from the oils of tarragon, fennel, star-anise, etc., all of which contain *anethole* or anise-camphor, $C_6H_4(OCH_3)C_3H_5$, which yields anisic acid on oxidation.

Anisic acid may also be prepared by several synthetical reactions.

Anisic acid forms long monoclinic needles or prisms, m. p. 184°, b. p. 280°. It is soluble in about 2,500 parts of cold water, tolerably soluble in boiling water and readily in alcohol.

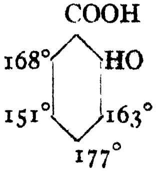
When heated with hydriodic or concentrated hydrochloric acid, or when fused with potassium hydroxide, anisic acid is converted into *p*-hydroxybenzoic acid. When distilled with baryta, it is decomposed into anisole and carbon dioxide.

The sodium salt and phenyl ester of anisic acid are employed in the treatment of neuralgia and rheumatism.

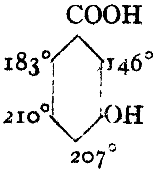
Hydroxy-phenyl-acetic Acids, $C_6H_4(OH).CH_2.COOH$.—The ortho-modification melts at 144°–145°, the meta- at 129°, and the para- at 148°. The last-named has been found in urine, and is formed in the putrefaction of albumin and synalbin. All 3 isomerides give a violet coloration with ferric chloride. When heated with lime they yield carbon dioxide and the corresponding isomeride of cresol, $C_6H_4(OH).CH_3$.

Hydroxy-toluic Acids.—Ten modifications of hydroxy-toluic acid are possible, and all have been prepared. The following arrangement shows the m. p. of these isomerides. Thus the acid having the COOH, OH, and CH_3 groups in the positions 1:2:3 melts at 163°, whilst when the methyl group occupies the para-position, the other groups remaining as before, the compound melts at 177°.

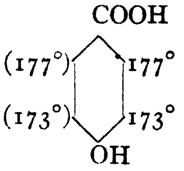
Ortho-derivatives



Meta-derivatives



Para-derivatives



Those hydroxy-toluic acids which have the hydroxyl group in the *ortho*-postion (1:2) in reference to carboxyl are true homologues of salicylic acid, and are known as *homosalicylic* or *cresotic acids*.[1] They give a violet coloration with ferric chloride, dissolve with facility in cold chloroform, and volatilise readily in a current of steam. The cresotic acids are liable to occur as objectionable impurities in commercial salicylic acid (see page 475).

Of the 4 acids having the carboxyl and hydroxyl groups in the *meta*-position (1:3) relatively to each other, 3 give pale brown precipitates with ferric chloride, soluble more or less readily in excess of the reagent to dark brown solutions. The 1:3:4 acid gives no reaction with ferric chloride. The meta acids are not attacked by heating with concentrated hydrochloric acid at about 200°, but yield cresols when heated with lime. They are volatile with difficulty or not at all (1:3:5 acid) in a current of steam.

The 2 homologues of *p*-hydroxybenzoic acid crystallise in small needles containing $\frac{1}{2}H_2O$, which become anhydrous at 100°. They volatilise more or less in a current of steam, but give no reaction with ferric chloride and are not soluble in cold chloroform.

The table on the following page exhibits the leading characters of the isomeric hydroxy-toluic acids:

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[1] Some chemists in expressing the constitution of the hydroxy-toluic acids, assign a constant position 1 to the methyl-group, following with the hydroxyl and carboxyl groups in the order named. Such a plan materially alters the nomenclature of the acids, and fails to exhibit the analogy of properties and reactions set forth in the text.

ISOMERIC HYDROXY-TOLUIC ACIDS

Acid. COOH:-OH:Me	M. p., °	On heating with hydrochloric acid	Reaction with ferric chloride	Solubility in cold chloroform	Crystalline form	M. p. of methyl ethers	Observations
Ortho-.							
1:2:3	163	*o*-cresol at 210°.	Deep violet colour.	Readily.	Long flat needles or rhombic prisms.	85°	*o*-cresotic acid; poisonous.
1:2:4	177	*m*-cresol at 170°.	Deep violet colour.	Moderately.	Hard white needles or prisms.	103°	*m*-cresotic acid.
1:2:5	151	*p*-cresol at 180°.	Violet-blue colour.	Readily.	Long needles and rhombic prisms.	67°	*p*-cresotic acid; gives *p*-cresol on heating with lime.
1:2:6	168	*m*-cresol at 200°.	Blue-violet colour.	Readily.	Long needles.	......	....
Meta-.							
1:3:2	145°–146°	Not attacked at 210°.	Yellowish-brown colour.	Slight.	Long vitreous needles.	146°	Gives *o*-cresol when heated with lime.
1:3:4	207	Not attacked at 270°.	No reaction.	Insoluble.	Long needles.	156°	Gives *o*-cresol when heated with lime.
1:3:5	208	Not attacked at 230°.	Fawn ppt. dissolving in excess with dark brown colour.	....	Stellate groups of needles.	93°	Symmetrical hydroxytoluic acid. Gives *m*-cresol when heated with lime. Not volatile with steam.
1:3(5)6(2)	183°–184°	Not attacked at 220°.	Light brown ppt. sol. in much water.	Nearly insoluble.	Prisms and needles.	......	....
Para-.							
1:4:2(6)	177	*m*-cresol at 200°.	None.	Insoluble.	Small needles containing ½H_2O.	176°	....
1:4:3(5)	173	*o*-cresol at 180°.	None.	Insoluble	Small needles containing ½H_2O.	193°	....

Cresotic acid, $C_6H_3(CH_3)(OH).COOH$, may be prepared from cresol by Kolbe's method for the manufacture of salicylic acid from phenol, the modification of cresotic acid obtained depending on the isomeride of cresol employed for the process. It is to the presence of cresols in the carbolic acid employed in Kolbe's process that the contamination of commercial salicylic acid by the isomeric cresotic acids is due (page 475). The 3 isomerides of cresotic acid present a close resemblance to salicylic acid and to each other, but differ in their m. p., therapeutic action and the modification of the cresol yielded on heating under pressure with hydrochloric acid or distillation with lime.

According to M. Charteris (*Pharm. J.*, 1890, [iii], **21**, 436), *m*-cresotic acid is devoid of physiological action, but both the *o*- and *p*-modifications possess marked toxic properties. Charteris found *p*-cresotic acid to produce marked paralytic symptoms in rabbits when injected hypodermically, the effect becoming more marked when the poison was given in conjunction with salicylic acid, 10 grains of the mixture causing convulsions and death.

The foregoing conclusions of Charteris have had grave doubt thrown on them by the observations of others. Thus Egasse has drawn attention to the advantages of *p*-cresotic acid as an antipyretic. Demme regards it as inferior to salicylic acid as an antipyretic, but free from some of the objections to the latter, being better tolerated by the digestive organs. Demme considers *p*-cresotic acid the most effectual and least objectionable of the 3 isomerides. *m*-Cresotic acid he regards as less active, whilst *o*-cresotic acid possesses decided toxic properties, causing paralysis of the cardiac muscle. According to Demme, also, the observed ill effects are attributable to the presence of *o*-cresotic acid in the preparations used. Sodium *p*-cresotate may be taken to the extent of 3 to 4 grm. without any ill effect resulting. It did not influence the temperature or occasion gastric disturbance (*Bull. Therap.*, 1892, **122**, 85; abst. *Pharm. J.*, 1892, [iii], **22**, 694).

A solution of cresotic acid has received application as a bateing liquid in tanneries. It is stated to have the advantage over other acids of exerting an antiseptic action on the skins, and so preserving instead of destroying them (J. Hauff, *J. Soc. Chem. Ind.*, 1889, **8**, 974). As it rapidly and easily dissolves the lime salts, it softens and swells the hides in a very satisfactory manner.

DIHYDROXYBENZOIC ACIDS AND THEIR ALLIES

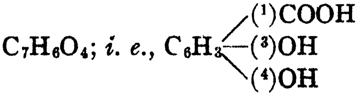
By the substitution of 2 hydroxyl-groups for 2 of the remaining hydrogen atoms of the benzene-nucleus in benzoic acid, a series of dihydroxyphenyl-carboxylic or dihydroxy-benzoic acids are obtained, of which protocatechuic acid is the type.

The dihydroxybenzoic acids may be obtained (among other reactions by heating the corresponding dihydroxybenzenes (hydroxyphenols) with solutions of alkali carbonates, the reaction occurring with much greater facility than the formation of salicylic acid by Kolbe's process (page 476). By further heating, the dihydroxybenzoic acids split up into the corresponding hydroxyphenols and carbon dioxide.

ISOMERIC DIHYDROXYBENZOIC ACIDS $C_6H_3(OH)(OH)COOH$

	Acid	COOH OH OH	M p, °	Colour with ferric chloride	Phenolic product, on heating
o-Hydroxyphenyl-carboxylic acids	Protocatechuic	1 . 3 4	194°–195°	Green	Catechol.
	Catechol-carboxylic	1 . 2 3	204°	Blue	Catechol
	α-Resorcylic.	1 : 3 . 5	222 (233)	No colour	Resorcinol
	β-Resorcylic	1 : 2 . 4	213	Dark-red	
m-Hydroxyphenyl-carboxylic acids	γ-Resorcylic.	1 : 2 : 6	148 (decomp)	Violet, blue with excess	Resorcinol. Resorcinol.
p-Hydroxyphenyl-carboxylic acid	Gentisinic, or hydroxysalicylic	1 . 2 : 5	200	Blue	Quinol

Protocatechuic acid. Ortho-dihydroxybenzoic acid



$$C_7H_6O_4;\ i.\ e.,\ C_6H_3\begin{cases}(^1)COOH\\(^3)OH\\(^4)OH\end{cases}$$

Protocatechuic acid occurs naturally in the fruit of *Illicium religiosum*. It results from the fusion of various organic substances with alkali hydroxides. Catechin and maclurin by similar treatment yield phloro-glucinol. Many resins give *p*-hydroxybenzoic acid in addition, whilst gum benzoin gives protocatechuic and benzoic acids. The largest yield of protocatechuic acid is stated to be obtainable from gum kino (*Annalen*, 1875, **177**, 188). It may be prepared synthetically by heating catechol to 130° with a solution of sodium or ammonium carbonate. On dry distillation or when heated to 330° to 350° with potassium or sodium hydroxide, the reverse action occurs, the protocatechuic acid splitting up into catechol and carbon dioxide.

Protocatechuic acid forms thin monoclinic prisms or tufts of needles containing one molecule of water, which is lost at 100°. It melts, when quite anhydrous, at 194° to 195°[1] and at a higher temperature is resolved into carbon dioxide and catechol, $C_6H_4(OH)_2$. Protocatechuic acid dissolves in 53 parts of cold water, and in 3.5 parts at 80°. It is very soluble in alcohol, less so in ether, and almost insoluble in benzene, even when boiling. It is extracted from its aqueous solution by agitation with ether or petroleum spirit.

Reactions.—An aqueous solution of protocatechuic acid is coloured an intense bluish-green by ferric chloride (avoiding excess), the colour being changed to blue and afterwards to dark red on adding a very dilute solution of sodium carbonate. A neutral solution of a protocatechuate gives a violet coloration with ferrous sulphate.

Protocatechuic acid gives a white precipitate with lead acetate, and reduces ammonio-nitrate of silver when heated, but has no effect on Fehling's solution.

On boiling protocatechuic acid with aqueous arsenic acid it yields *diprotocatechuic acid*, $C_{14}H_{10}O_7$, a substance closely resembling digallic acid (tannin), but giving a green coloration with ferric chloride.

The salts of protocatechuic acid are unimportant, but the esters, vanillic acid, piperonylic acid, and veratric acid have some interest (page 538).

Estimation.—Imbert stated (*Compt. Rend.*, 1900, **130**, 37) that protocatechuic acid is monobasic towards phenolphthalein. According to Massol, however, the acid requires 1.5 molecules for neutralisation (*Bull. Soc. chim.*, 1900, [iii], **23**, 331). But the acid used by the latter author was yellow, and had m. p. 199° (instead of 194–195°), and Imbert, on repeating his experiments, confirmed his original statement (*Bull. Soc. chim.*, 1900, [iii], **23**, 832). The end-point is somewhat obscure. Towards Poirrier's blue protocatechuic acid is dibasic.

Homologues of Protocatechuic Acid.—Besides the important class of tannins giving green colorations with ferric salts (Vol. 5), the following homologues and derivatives of protocatechuic acid have a practical interest:

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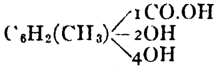
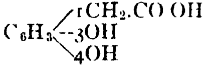
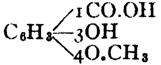
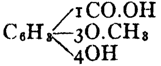
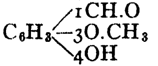
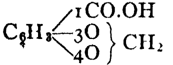
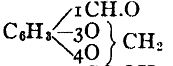
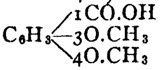
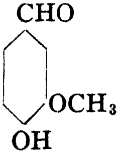
[1] This seems to be the correct m. p., but Hlasiwetz gives 199° and Schmidt and Barth give 194°.

Name	Formula	M. p., °	Coloration with ferric chloride
Orsellinic acid. Dihydroxy-*o*-toluic acid.	 $C_6H_2(CH_3)\left\langle\begin{matrix}1CO.OH\\2OH\\4OH\end{matrix}\right.$	176	Violet.
a-Homoprotocatechuic acid...	 $C_6H_3\left\langle\begin{matrix}1CH_2.CO.OH\\3OH\\4OH\end{matrix}\right.$	127	Green.
iso-Vanillic acid. *p*-Methylprotocatechuic acid.	 $C_6H_3\left\langle\begin{matrix}1CO.OH\\3OH\\4O.CH_3\end{matrix}\right.$	250	Yellow.
Vanillic acid. *m*-Methylprotocatechuic acid.	 $C_6H_3\left\langle\begin{matrix}1CO.OH\\3O.CH_3\\4OH\end{matrix}\right.$	207	No colour.
Vanillin. *m*-Methylprotocatechuic aldehyde.	 $C_6H_3\left\langle\begin{matrix}1CH.O\\3O.CH_3\\4OH\end{matrix}\right.$	80°–81°	Blue.
Piperonylic acid. Methylene-protocatechuic acid.	 $C_6H_3\left\langle\begin{matrix}1CO.OH\\3O\\4O\end{matrix}\right.\!\!\left.\begin{matrix}\\ \\ \end{matrix}\right\}CH_2$	228	
Piperonal. Methylene-protocatechuic aldehyde.	 $C_6H_3\left\langle\begin{matrix}1CH.O\\3O\\4O\end{matrix}\right.\!\!\left.\begin{matrix}\\ \\ \end{matrix}\right\}CH_2$	37	
Veratric acid. Dimethylprotocatechuic acid.	 $C_6H_3\left\langle\begin{matrix}1CO.OH\\3O.CH_3\\4O.CH_3\end{matrix}\right.$	179	Yellow.

Vanillin. $C_8H_8O_3$; *i. e.*,



Vanillin is the aldehyde of vanillic or methylprotocatechuic acid. It is the chief odoriferous principle of vanilla pods or *vaniloes*, the fruit of *Vanilla planifolia*, from which it was isolated in 1858. It also occurs in traces in cloves, beetroot, Siam benzoin, asafœtida, and asparagus, and its presence in the wood of certain trees has frequently been noted. (See Von Lippmann, *Ber.*, 1904, **37**, 4521.)

Vanilla is the fruit or pod of *Vanilla planifolia*, var. *aromatica*, an orchid grown in Mexico, Bourbon, the Seychelles, Fiji, etc. Its cultivation has become, to a certain extent, restricted since vanillin has been produced artificially; but the superior aroma and flavour of the natural product prevent the artificial vanillin from wholly superseding it.[1]

W. Busse (*Arb. Kaiserl. Ges.*, 1898, **15**, 1) found 2.16% of vanillin in German East African vanilla; 1.48% in Ceylon pods; and 1.55 and 2.02% in Tahiti vanilla. Tiemann and Haarmann (*Ber.*, 1875, **8**, 1115) found in the best Mexican pods 1.69 and 1.86 of vanillin; in Bourbon, 1.91 to 2.90; and in Java pods 2.75% of vanillin.

Busse holds that there is no relation between the proportion of vanillin contained in the fruit and the value of the sample for flavouring purposes, and that the aroma and flavour of vanilla are not wholly due to vanillin. Tiemann and Haarmann found that on distilling the ethereal extract of vanilla, from which the vanilla has been removed by sodium hydrogen sulphite, an oily substance of very offensive odour remained. Much less was obtained from Mexican vanilla than from Java or Bourbon pods.

In the variety of West Indian vanilla called *vanillone* the vanillin (from 0.4 to 0.7%) is associated with another substance, which is probably benzaldehyde. Vanillone has long been used for preparing "essence of heliotrope," but this is now made by adding a small quantity of benzaldehyde (artificial) to artificial vanillin, when, after some time, the mixture acquires the exact odour of the natural white heliotrope.

Some varieties of vanilla contain *vanillic acid*, which was apparently mistaken for benzoic acid by the earlier investigators.

Inferior or exhausted vanilla is occasionally dusted over with crystals of benzoic acid, which gives it the frosted appearance regarded as characteristic of vanilla of good quality. If a little of the crystalline matter be added to an alcoholic solution of phloroglucinol previously mixed with an equal volume of hydrochloric acid, a magnificent red colour is produced in presence of vanillin.

Vanillin is now produced artificially on a considerable scale, by a variety of methods, some of which have proved very lucrative.[2]

Practically the whole of the artificial vanillin of commerce is now made from eugenol, a phenol contained in oil of cloves and oil of cinnamon leaves, by acetylating it with acetic anhydride and oxidising the acetate with potassium permanganate and sulphuric acid (Bertram D. R. P. 63007; Sommer D. R. P. 122851; Schering D. R. P. 82816; etc.).

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[1] The substance to which the odour of vanilla is due does not appear to exist in the fruit when gathered, but is developed during the "curing" operation by a process of fermentation (compare Lecomte, *Comp. rend.*, 1901, **133**, 745). The greater part of the vanillin is contained in the fruit in the form of a glucoside, from which free vanillin can be obtained by the action of emulsin or dilute acids.

[2] In 1876, the price of vanillin was fully £10 per ounce. At present it may be bought for 3s. or less.

Vanillin crystallises in stellate groups of colorless needles, melts at 80° to 81°, and sublimes when cautiously heated. It has a pleasant aromatic taste and odour resembling vanilla. Vanillin dissolves sparingly in cold water, more freely in hot, and readily in alcohol and ether.

Commercial vanillin is not infrequently adulterated to a considerable extent (*e. g.*, 50%) with acetanilide (antifebrin), an addition of which lowers the m. p. of the sample. The admixture may be detected by heating the substance to 60° with a 5% solution sodium hydroxide, when aniline is formed and may be detected by the usual tests. A quantitative separation of vanillin and acetanilide may be effected by dissolving the mixture in ether and shaking the liquid with a concentrated aqueous solution of sodium hydrogen sulphite, which dissolves the vanillin only. The amount of acetanilide present in vanillin may also be deduced from the nitrogen in the sample (L. F. Kebler, *Amer. J. Pharm.*, 1902, **74**, 12).

Sugar is occasionally met with as an adulterant of vanillin. It may be detected by its insolubility in ether or chloroform.

In America, vanillin is sometimes adulterated with *benzoic acid*, and occasionally that acid simply flavoured with vanillin has been substituted for the latter substance. The 2 substances may be separated by dissolving the sample in ether and shaking the liquid with sodium hydrogen sulphite solution, which will remove the vanillin, leaving the benzoic acid dissolved in the ether.

Kebler has met with vanillin adulterated with, or substituted by, acetyl-*iso*-eugenol, the direct antecedent of vanillin in its synthetic production from *iso*-eugenol. One adulterated sample contained only a little vanillin, added to give the characteristic odour. Acetyl-*iso*-eugenol melts at 79° to 80°, and vanillin at 80° to 81°. The adulterant was detected by its crystalline form, abnormal solubility in various solvents, and by the presence of the acetyl-group. Strong sulphuric acid gave a beautiful red colour, whereas a lemon-yellow colour is yielded by pure vanillin. The amount of vanillin was estimated by the Hess and Prescott method (page 550).

Ritsert's tests, adopted by the United States Bureau of Chemistry, are as follows: One to three drops of a solution of chloride of lime (1:200) are added carefully to a portion of the extract in such a manner that the two liquids do not mix. The formation of a beautiful blue colour at the junction of the two liquids indicates the presence of acetanilide.

(2) A small drop of potassium permanganate solution, when added to a second portion, gives a clear green colour if any appreciable amount of acetanilide is present.

(3) A third portion is mixed with a small drop of a 3% solution of chromic acid. Acetanilide gives a yellowish green solution, changing to dark green after 5 minutes, and forming a dark blue precipitate on addition of a drop of potassium hydroxide solution.

These tests are only conclusive when taken in conjunction with the m. p.

According to Lehmann (*Chem. Zeit.*, 1914, **38**, 388, 402) vanillin from clove oil has a different melting point from that from guaiacol. He states that the adulteration of vanillin can be detected and its amount estimated by observations of the sintering point, the melting point as determined in the German Pharmacopœia (*i.e.*, the temperature at which the substance forms a continuous column of liquid containing solid particles) and the point of clear fusion. The more nearly pure the product, the smaller is the difference in temperature between the first sintering and complete liquefaction.

Reactions.—Vanillin has the constitution and characters of an aromatic aldehyde. It forms well-defined sulphite compounds, reduces ammoniacal silver solution, and responds to other general reactions for aldehydes. Heated with dilute hydrochloric acid (preferably under pressure to 200°) vanillin is resolved into methyl chloride and protocatechuic aldehyde; and when fused with potassium hydroxide is converted into protocatechuic acid.

By exposing moist and finely pulverised vanillin to the air it is oxidised to vanillic or methylprotocatechuic acid, $C_8H_8O_4$, which crystallises from ether in white laminæ, and gives no colour reaction with ferric chloride.

By reducing vanillin in dilute alcoholic solution with sodium amalgam, vanillyl alcohol, $C_6H_3(OH)(OCH_3),CH_2OH$, is produced, which forms prisms m. p. 115°. Vanillin has an acid reaction and forms salts with bases.

On heating vanillin with hydrochloric acid and phloroglucinol a characteristic red colour is produced.

On rubbing together vanillin, resorcinol, and hydrochloric acid, a deep bluish-violet coloration is observed, which vanishes after a time (Etti, *Monatsh.*, 1882, **3**, 637). A 1% solution of vanillin in hydrochloric acid mixed with an equal volume of sulphuric acid, gives with a few drops of a liquid containing even 0.01% of acetone, a violet colour on heating at 100° for 15 minutes.

If a little thiophene and concentrated sulphuric acid be added to an alcoholic solution of vanillin, the liquid acquires a green to bluish-green coloration (A. Ihl, *Chem. Zeit.*, 1890, **14**, 1707).

Besides its agreeable odour, vanillin is characterised by the bluish-violet coloration produced in its solution on addition of ferric chloride. On heating the liquid, *dehydro-divanillin*, $C_{12}H_4(OH)_2(COH)_2(OCH_3)_2$, separates in fine white needles, m. p. 304°, and sparingly soluble in water, alcohol, ether, chloroform, and benzene, but readily soluble in alkalis (Tiemann, *Ber.*, 1885, **18**, 3493).

According to E. P. Haussler (*Zeit. anal. Chem.*, 1914, **53**, 691–695; 1915, **54**, 104) when albumin, casein, peptone, fibrin or pepsin is treated with a small quantity of dilute alcohol and evaporated with the addition of a small quantity of vanillin a yellow coloration is obtained which changes to violet when treated with hydrochloric acid and again evaporated.

To distinguish vanillin from heliotropin A. Labat describes the following test (*Bull. Soc., pharm. Bordeaux*, 1919, **57**, 259–260). To 2 c.c. of sulphuric acid (sp. gr. 1.84) is added 0.1 c.c. of the alcoholic solution to be tested and 0.1 c.c. of an alcoholic solution of gallic acid (20%) and the mixture boiled on a water-bath for 2 or 3 minutes. The liquid turns yellowish-brown or brown if vanillin is present, but acquires a blue or emerald green colour in the presence of heliotropin.

Detection.—Lecomte has proposed a test for vanillin in quinine wines consisting of mixing an ethereal extract of the wine with dilute hydrochloric acid and adding an alcoholic solution of phloroglucinol; a red zone appears at the junction of the two liquids within about 10 minutes if vanillin is present. Chauvin, however, points out (*Ann. Falsif.*, 1914, **7**, 420) that the reaction is also given by furfural and its derivatives, that these are frequently present in the wines used in the preparation of quinine wines, and that the test is not, therefore, characteristic of vanillin.

A. Stocky (*Zeitsch. Nahr. Genussm.*, 1900, **3**, 233) isolated vanillin from a sample of wine vinegar suspected to contain it, by evaporating a large volume of the liquid to dryness with calcium carbonate, extracting the residue with ether, and evaporating the ethereal solution. After repeatedly crystallising the residue thus obtained from alcohol it was identified as vanillin by the formation of a metallic mirror with an ammoniacal silver solution, and its reaction with phloroglucinol and hydrochloric acid.

Estimation.—Vanillin may be extracted from aqueous liquids containing it by acidifying and agitating with ether. It may then be separated from many substances simultaneously extracted by agitating the ethereal solution with a semi-saturated solution of sodium hydrogen sulphite.

J. Hanuš has described a method of estimating vanillin based on its conversion into a hydrazone of suitable properties (*Zeitsch. Nahr Genussm.*, 1900, **3**, 531).

Owing to the instability of *p*-bromophenyl hydrazine and the interference of foreign substances (especially fats), however, he has abandoned the use of hydrazines in favour of the following process (*Zeitsch. Nahr. Genussm.*, 1905, **10**, 587): The solution of vanillin (approximately 0.25%) is treated with 50% excess of a 2% solution of *m*-nitrobenzoylhydrazide in hot water. The flask containing the mixture is closed with a cork and allowed to stand, with occasional shaking, for 24 hours, when the smell of vanillin should have disappeared. Vanillin solutions of the above strength are precipitated immediately, but more dilute solutions give no cloudiness until after 5 or 10 minutes. The precipitate is collected on a tared Gooch crucible, washed with cold water until the filtrate no longer reduces ammoniacal silver nitrate solution, and dried for 2 hours at 100 to 105°. After 10 minutes, heating at this temperature, the precipitate turns brown and becomes glassy, but at the end of a further 15 minutes it regains its original appearance. The weight of the precipitate multiplied by 0.4829 gives the weight of vanillin.

For the estimation in vanilla, 3 grm. of the powdered sample are extracted for 3 hours with not more than 50 c.c. of ether. The extract is evaporated at 60°, at which temperature no appreciable amount of vanillin is volatilised, the residue dissolved in a small quantity of ether, filtered into a conical flask and the filter washed with ether. The filtrate and washings are evaporated, the residue warmed with 50 c.c. of water to form an emulsion, and precipitated as described above. Before filtration of the precipitate the liquid is shaken with petroleum spirit to dissolve any fat present, and the solid collected in the Gooch crucible is washed with the same solvent. The method is inapplicable in the presence of piperonal or other aldehydes. Hanuš states that his methods are applicable in all cases where an aqueous solution of the vanillin can be prepared, and claims that they have the advantage over Welman's method (titration with alcoholic potassium hydroxide) of being unaffected by the presence of vanillic acid.

A more rapid but less accurate method of estimating vanillin in vanilla is as follows: A known weight (20 to 50 grm.) of the pods should be ground up with sand, and the mixture extracted with ether. The filtered liquid is shaken with a saturated solution of sodium hydrogen sulphite, diluted with an equal volume of water, and the ethereal layer separated. The sulphite solution is then treated with dilute sulphuric acid, and the sulphurous acid liberated driven off by passing a current of carbon dioxide or steam. The vanillin is then extracted from the acid liquid by agitating with ether, which is separated, cautiously evaporated, and the residual vanillin weighed.

Certain species of vanilla contain *piperonal* as well as vanillin. No satisfactory method has hitherto been proposed for the separation of these 2 aldehydes, and any process for the estimation of vanillin in presence of piperonal must depend on the reactions of the free hydroxyl-group present in vanillin but not in piperonal. Certain colour-reactions fall under this head, *e. g.*, with mercurous nitrate, *p*-nitrodiazobenzene or ferric salts, but these are hardly applicable for quantitative purposes. Hence J. Hanuš (*Zeitsch. Nahr. Genussm.*, 1900, 3, 657) recommends the following procedure: A volume of liquid, estimated to contain from 0.02 to 0.15 grm. of vanillin, is placed in an Erlenmeyer flask of 150 c.c. capacity, and 10 c.c. of a 10% solution of platinic chloride added. The volume is then made up to 50 c.c. with water (with more than 0.06 grm. of vanillin it may be made up to 100 c.c. if desired). The flask is then placed in a hot-water oven kept at a temperature of 70° to 80° and allowed to remain there for 1 hour. It is then removed and allowed to cool for 1 hour longer. The condensation product, consisting of grey needles free from mineral matter, is then filtered off in a Gooch crucible containing a layer of asbestos; it is washed with cold water, and dried at 100° to 105° to constant weight (about 3 hours). The quantity of vanillin, x, is calculated from the weight of the product, y, by one of the following formulæ: $x = \frac{y + 15.7}{0.97}$ (for 50 c.c.), or $x = \frac{y + 38.25}{1.04}$ (for 100 c.c.). The presence of piperonal has very little effect on the estimation of vanillin by the above method.

A new gravimetric method of estimating vanillin in vanilla extracts has been described by A. W. Dox and G. P. Plaisance (*Amer. J. Pharm.*, 1916, **88**, 481–484; 1919, **91**, 167–170). This depends on the precipitation of the vanillin as 3-methoxy-4-hydroxybenzalmalonylthiourea by the reaction with thiobarbituric acid. 25 c.c. of the vanilla extract are de-alcoholised and then diluted to 50 c.c. with lead acetate solution. After standing for a few hours at 37° the mixture is filtered, 40 c.c. of the filtrate are treated with a quantity of concentrated hydrochloric acid sufficient to make the volume up to 50 c.c. and the acidity up to 12%, the lead chloride is filtered off, and 40 c.c. of this filtrate are treated with thiobarbituric acid in 12% hydrochloric acid solution. The precipitate is collected after 18 hours, washed with 50 c.c. of 12% hydrochloric acid, then with 20 c.c. of water, dried at 98° and weighed. To the weight of the precipitate obtained 0.0026 grm. must be added as a solubility correction. The method cannot be applied to artificial extracts coloured with caramel, since the latter contains furfural derivatives and thiobarbituric acid is a precipitant for all aromatic aldehydes. A sensitive test for caramel consists in treating the extract, after clarification and removal of lead chloride, with phloroglucinol, which gives a brown precipitate with caramel. In the absence of the latter the vanillin gives a pink precipitate.

A. Moulin (*Bull. Soc. chim.*, 1903, [iii], **29**, 278) has devised a colorimetric method for the estimation of vanillin in vanilla, based upon the conversion, by nitric acid, of the $—C_6H_3.OCH_3$ group in vanillin into methyl picrate.

The author claims that the method is very delicate, that the results agree with those given by the gravimetric methods, and that a difference of tint corresponding to 0.005 grm. of vanillin can be readily observed.

Another colorimetric method of estimating vanillin has been published by Folin and Denis (*J. Ind. Eng. Chem.*, 1912, **4**, 670). 5 c.c. of the flavouring extract are mixed with 75 c.c. of water and 4 c.c. of a solution containing 5% each of basic lead and normal lead acetate, and diluted to 100 c.c. with water. The mixture is rapidly filtered, and 5 c.c. of the filtrate are transferred to a 50 c.c. flask, 5 c.c. of a standard solution of vanillin (1 mg. in 10 c.c.) being placed in another similar flask. 5 c.c. of a phosphotungstic-phosphomolybdic acid reagent are added to each flask, and after being shaken and allowed to stand for 5 minutes the solutions are made up to 50 c.c. with a saturated solution of sodium carbonate and well mixed. After standing for 10 minutes the solutions are filtered and the colours of the filtrates compared in a Duboscq colorimeter. The reagent is prepared by boiling 100 grm. of pure sodium tungstate and 20 grm. of phosphomolybdic acid (free from nitrates and ammonium salts) with 100 grm. of syrupy (85%) phosphoric acid and 700 c.c. of water for 1½–2 hours, cooling, filtering if necessary, and diluting to 1 litre. Coumarin, extract of tonka beans and acetanilide do not give the rich blue colour produced by vanillin, and sugar, caramel, and glycerol do not interfere with the test:

In place of the dilute standard vanillin solution given above, Harder (*J. Ind. Eng. Chem.*, 1913, **5**, 619) recommends a stronger one—2 grm. in 200 c.c. of 90% alcohol—as being more stable.

Hubbard (*J. Ind. Eng. Chem.*, 1912, **4**, 669) has found the following disadvantages in the official United States method for the colorimetric estimation of vanillin. There is a difficulty in getting the maximum coloration; the original method of adding the ferrous sulphate first gives a deeper colour than the present one where the bromine is added first. It is difficult to add only enough lead cream (lead hydroxide) to decolorise the solution, and when different quantities are added the depth of colour subsequently obtained varies. Dilution of the sample influences the colour, Much larger amounts of ferrous sulphate are necessary in comparison with bromine water to produce a maximum colour. Lead cream forms a yellow crystalline lead vanillin derivative, $(C_8H_7O_3)_2Pb$, which renders a quantitative estimation impossible in the presence of lead.

C. Estes has described (*J. Ind. Eng. Chem.*, 1917, **9**, 142–144) a colorimetric method of estimating vanillin which depends on the fact that this aldehyde, when heated with acid mercuric nitrate, solution gives a violet coloration which is characteristic of vanillin, and the intensity of the coloration is directly proportional to the quantity of this substance present. In the case of alcoholic vanilla extracts, 5 c.c. of the sample are placed in a 50 c.c. flask, 6 c.c. of water and 1.5 c.c. of the reagent (prepared by dissolving mercury in twice its weight of nitric acid of specific gravity 1.42 and diluting the solution with 25 times its weight of water) are added, the flask is placed in boiling water for 20 minutes, then cooled rapidly, its contents diluted to 50 c.c., filtered, and the coloration obtained compared with that given by a known amount of vanillin under the same conditions. The procedure is the same for non-alcoholic extracts except that only 1 c.c. of the reagent is required. The author claims that the results obtained agree with those found by the gravimetric method.

Another colorimetric method, depending on the coloration produced by vanillin when treated with *iso*butyl alcohol and concentrated sulphuric acid, is described by Th. von Fellenberg (*Mitt. Lebensmittel. Hyg.*, 1915, **6**, 267–274).

Both a volumetric and a gravimetric method of estimating vanillin are described by S. B. Phillips (*Analyst*, 1923, **48**, 367–373).

A refractometric method of estimating vanillin in vanilla-sugar has been described by P. Hasse (*Chem. Zeit.*, 1922, **46**, 233–234).

A micro-analytical method of estimating vanillin in foodstuffs has been described by F. Wohack (*Zeitsch. Nahr. Genussm.*, 1921, **42**, 290–298) and a method of estimating it in brandy by T. von Fellenberg (*Mitt. Lebensmittel, Hyg.*, 1922, **13**, 98–110).

In a research on extraction by means of immiscible solvents Marden (*J. Ind. Eng. Chem.*, 1914, **6**, 315) has found that 99.6% of the vanillin can be removed from a vanilla extract, which has been freed from alcohol, by shaking once with 20 c.c. and 3 times with 15 c.c. of ether (all the coumarin and about 93% of the acetanilide are simultaneously extracted). For the removal of the vanillin from the ethereal solution he states that the original method of Hess and Prescott (shaking 50 c.c. with 10 c.c. of 5% ammonia) is the best, as it removes all the vanillin and only 5% of the acetanilide and 3% of the coumarin.

From a study of methods of estimating aldehydes Feinberg (*8th Int. Cong. Appl. Chem.*, 1912, Sect. I, Orig. Comm., **1**, 187) concludes that for vanillin the iodine and bisulphite methods each give results amounting to 95.5% of the theoretical, whilst precipitation with *p*-bromophenylhydrazine and *p*-nitrophenylhydrazine give 99% and 100% (approx.) respectively.

It has been pointed out by H. J. Wichmann (*J. Assoc. Off. Agric. Chem.*, 1921, **4**, 479–482) that, whilst the vanillin may be either weighed direct, weighed after purification with petroleum spirit or sublimed at 105°, the first method gives high results, the second frequently low and in the third the error is small with ordinary vanilla extracts, but becomes considerable with concentrated flavourings, in which case a +5% correction should be applied.

A method of simultaneously estimating the lead number and the alcohol content of vanilla extracts has been described by H. J. Wichmann (*J. Ind. Eng. Chem.*, 1921, **13**, 414–418). A mixture of 175 c.c. of water, 25 c.c. of 8% normal lead acetate solution and 50 c.c. of vanilla extract is distilled, 200 c.c. of the distillate being collected and the alcohol-content calculated from its specific gravity. The residue in the distillation flask is diluted to 100 c.c. with water free from carbon dioxide, filtered, and 10 c.c. of the filtrate are mixed with 25 c.c. of water, 10 c.c. of dilute sulphuric acid and 100 c.c. of alcohol are added and the precipitated lead sulphate collected and weighed. A control estimation is made at the same time, water containing 5 drops of glacial acetic acid being used in place of the vanilla extract. The quantity of lead precipitated by the extract and expressed as grm. per 100 c.c. is the lead value; for genuine undiluted extracts it is not less than 0.55. Sugar, glycerol and coumarin do not interfere with the estimation; if added vanillin is present, it must be removed by extracting 50 c.c. of the sample with three successive quantities (50 c.c.) of a mixture of equal volumes of ether and petroleum spirit, the aqueous solution being then used for the estimation.

To detect small quantities of coumarin in factitious vanilla extracts Wichmann has described (*U. S. Dept. of Agric., Bureau of Chem.*, Circular No. 95, April 6, 1912) the following method: 25 c.c. of the extract are made slightly acid with sulphuric acid, 25 c.c. of water added and the whole distilled to dryness. 15–25 drops of potassium hydroxide solution (1:1) are added to the distillate, which is then rapidly evaporated to 5 c.c. and transferred to a test-tube. The water is now boiled off, and the residue fused to a colourless mass. When cold, the residue is dissolved in a few c.c. of water and made slightly acid with 25% sulphuric acid. The solution is distilled, when the salicylic acid formed from the coumarin during the potash fusion, passes over and may be detected by the addition of neutral ferric chloride solution to the distillate.

Dean (*J. Ind. Eng. Chem.*, 1915, **7**, 519) modifies Wichmann's method as follows: A de-alcoholised sample of the vanilla extract is treated with 5 c.c. of ammonia and extracted with 15 c.c. of ether; coumarin is dissolved by the ether, but vanillin, salicylic acid and saccharin remain in the aqueous layer. The ether extract is evaporated, the residue treated with 5 drops of 50% potassium hydroxide solution, dried, fused, dissolved in a few c.c. of water acidified with sulphuric acid, and extracted with chloroform. The chloroform solution is tested foi salicylic acid, formed from the coumarin, by means of ferric chloride.

The author points out that coumarin would interfere with Durand's test for saccharin unless it is removed by extraction with an immiscible solvent in the presence of ammonia.

In a more recent method Wichmann (*J. Ind. Eng. Chem.*, 1918, **10**, 536–537) proceeds as follows: 50 c.c. of the alcoholic extract are treated with lead acetate solution, diluted to 100 c.c., filtered and the excess of lead removed by the addition of dry potassium oxalate. The liquid is again filtered and 50 c.c. of the filtrate extracted with ether. The ethereal extract is treated with an excess of alcoholic potassium hydroxide solution and a few drops of phenolphthalein solution, and the vanillin salt removed by washing several times with 10 c.c. of water, the disappearance of the red coloration indicating when washing is complete. The ether is then evaporated and the residue of coumarin dried and weighed. The amount of the residue varies from 98 to 102% of the coumarin present.

L. Geret states (*Mitt. Lebensm. Hyg.*, 1920, **11**, 69–71) that 5% of coumarin in vanillin can be detected by the yellow turbidity produced on adding a 1% solution of iodine in 2 % potassium iodide solution.

Winton, Albright and Berry publish (*J. Ind. Eng. Chem.*, 1915, **7**, 516) analyses of 77 samples of vanilla extract prepared from vanilla beans of different varieties, grades, and lengths by the U. S. P. method. They found that the total acidity ranged from 30 to 52 c.c. of N/10 alkali per 100 c.c.; acidity other than that due to vanillin (by difference), 14–42 c.c. of N/10 alkali; total ash 0.22–0.43 grm. per 100 c.c.; soluble ash 0.18–0.36 grm.; alkalinity of total ash 30–54 c.c. N/10 acid; alkalinity of soluble ash 22–40 c.c. N/10 acid.

For the separation of *vanillin* and *coumarin*, as required in the analysis of mixed extracts of vanilla and Tonka beans, Hess and Prescott (*J. Amer. Chem. Soc.*, 1899, **21**, 256) recommend the following process: A weight of from 25 to 100 grm. of the extract is evaporated at 80°, water being added at intervals to keep the volume of the liquid constant until the alcohol has volatilised. Lead acetate is then added with agitation as long as a precipitate forms, when the liquid is filtered through asbestos and the precipitate washed with a little hot water. The cooled filtrate is agitated with ether, and the ethereal layer separated and agitated with dilute ammonia in portions of 2 c.c. This extracts the vanillin, whilst the coumarin remains dissolved in the ether, which is allowed to evaporate spontaneously. The residual coumarin is purified by solution in petroleum spirit and finally weighed. The m. p. (67°) and characteristic odour are sufficient for its identification. The vanillin may be recovered by slightly acidifying the ammoniacal solution with hydrochloric acid, extracting with ether, and evaporating cautiously. After purification by solution in boiling petroleum spirit, the product should be pure vanillin, m. p. 80° to 81°. After weighing, colour-tests may be applied for the identification of vanillin, bearing in mind that phenolic substances giving colorations with ferric salts are liable to be present. Chloroform may be advantageously substituted for ether in the above process, which Hess and Prescott consider preferable to the alkali hydrogen sulphite method.

Winton and Silvermann (*J. Amer. Chem. Soc.*, 1902, **24**, 1128), recommend the above process, but use a 2% solution of ammonia instead of 10% as prescribed by Hess and Prescott, and they also prefer to weigh the vanillin and coumarin before dissolving in petroleum spirit. Any insoluble matter, which is usually insignificant in amount, may afterwards be weighed separately and allowed for if necessary. 6 extracts prepared by Winton and Silvermann from different grades of vanilla pods by the formula of the United States Pharmacopœia (100 grm. of pods per litre of extract) had a sp. gr. ranging from 1.0104 to 1.0166, and contained vanillin, from 0.06 to 0.22% and cane-sugar, about 20%.

For details of the methods of analysis see *Connecticut Agric. Exp. Stat. Rep.*, 1901, **25**, 149 (*J. Soc. Chem. Ind.*, 1902, **21**, 1300) and *Bul* 107, *Bureau of Chem.*, *U. S. Dept. of Agric.* Winton and Bailey have further modified the process by diluting the sample to 3 times its volume and evaporating at 70° to the original bulk, and repeating this process in order to expel alcohol without losing vanillin. The coumarin, after isolation, is extracted with very light petroleum (b. p. 30 to 40°) which leaves undissolved any acetanilide present. The latter may be recognised by the usual tests (*J. Amer. Chem. Soc.*, 1905, **27**, 719).

Essence of Vanilla.—Under this name, an alcoholic extract of vanilla beans is largely employed for flavouring purposes. Much of the so-called "essence," however, is merely an alcoholic solution of artificial vanillin, coloured with caramel (sometimes with an admixture of artificial coumarin). Genuine extract of vanilla pods contains a resin of dark red or brown colour, soluble in 50% alcohol, but precipitated on further dilution. Hence, when weaker spirit is used for preparing vanilla extract, potassium hydrogen carbonate or other alkali is used to effect solution of the resin, but the flavour of the preparation is prejudicially affected thereby. Presence of resin, as indicated by precipitation on dilution with water, is more or less indicative of a genuine extract, whereas the presence of caramel and coal-tar dyes points to the vanillin being artificial.

Doherty (*J. Roy. Soc., New S. Wales*, 1914, **47**, 157) expresses the opinion that the most trustworthy method of estimating vanillin in essence of vanilla is to distil the essence, extract the vanillin from the residue with ether, combine with sodium hydrogen sulphite, filter, decompose with sulphuric acid, extract with chloroform, evaporate, dry *in vacuo* and weigh. He also gives the following quick method: 1 c.c. of the vanilla essence is extracted with ether, the extract evaporated over water, and the aqueous solution filtered and diluted to 50 c.c. in a Nessler glass. 10 drops of freshly prepared bromine water, and 10 drops of 10% ferrous sulphate solution are then added and the colour matched against that given by a 0.2% vanillin solution under the same conditions.

The tests of the Bureau of Chem., U. S. Dept. of Agric., for the detection of these resins and caramel colour are as follows:

Vanillin, although the most important, is not the only fragrant principle of the vanilla bean and true vanilla extract. The bean also contains, among the many extractive matters which enter into the food value and fragrance of the extract, certain resins which can be identified by a number of reactions. If the latter give negative results, it is evident that the extract was not made from vanilla beans.

Vanilla beans contain from 4 to 11% of these resins, which vary from dark red to brown in colour and give rise to about one-half of the colour of the extract.

For the detection of the resins the extract is treated as follows: 50 c.c. of the sample to be examined are placed in a glass dish, and heated on a water-bath to expel the alcohol. When the latter has evaporated, the residue is diluted to the original volume with hot water. Provided alkali has not been used in the preparation of the extract, the resins will appear as a flocculent red or brown residue. The liquid is acidified with acetic acid to remove bases from the resins, the whole of which separate after a short time, leaving a partly decolorised, clear, supernatant liquid. The resin is collected on a filter and washed with water, the filtrate being reserved for further tests. When a portion of the filter with the attached resin is treated with a small quantity of dilute potassium hydroxide solution, the resin dissolves to a deep red solution which is precipitated by acids.

Unlike most resins, that derived from vanilla beans, when dissolved in alcohol, gives a solution of which the colour is very little changed by either hydrochloric acid or ferric chloride.

A portion of the filtrate from which the resin was separated, gives a precipitate with a solution of basic lead acetate, which is so bulky as almost to solidify. The filtrate from this precipitate is almost colourless.

Another portion of the filtrate from the resin may be tested for tannin with a solution of gelatin. Tannin occurs in the vanilla bean in varying but small quantities, a large proportion should not be found.

The presence of **caramel** as a colouring matter is indicated if, on shaking the bottle of vanilla extract, the bubbles formed are of a bright caramel colour, and retain this colour until all of them have disappeared. The colouring matter present in vanilla or tonka extracts is almost completely removed when the de-alcoholised extract is treated with basic lead acetate solution. If caramel is present, the filtrate and precipitate, if any, have the characteristic red-brown colour of this substance.

An imitation extract of vanilla made from Tonka beans is sometimes substituted in America for true vanilla extract. H. Leffmann distinguishes between them by evaporating the extract on the water-bath, redissolving the residue in a little water, acidifying the solution slightly, and shaking with ether. The residue left on evaporating the ethereal layer is mixed with a very small amount of phloroglucinol and a drop of hydrochloric acid, and the mixture heated on the water-bath. Vanillin gives a red coloration, but coumarin does not. This test would not serve for the detection of Tonka beans in admixture with vanilla.

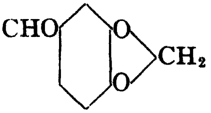
The following method of detecting coumarin (*U. S. Dept. Agric. Bur. Chem. Bull.* 107) is given on the authority of Albert E. Leach ("Food Inspection and Analysis," 2nd Ed., p. 858). A few of the crystals are dissolved in a small quantity of hot water, the solution filtered if necessary, and the filtrate treated with a few drops of N/10 solution of iodine in potassium iodide. In the presence of coumarin a brown precipitate will be formed, which, on stirring or shaking, collects in dark green flocks leaving a clear brown solution. The reaction is especially marked if the iodine reagent is applied with a glass rod to the solution to be tested on a white tile.

The following colorimetric method has been proposed by Moerk (*Amer. Jour. Pharm.*, 1891, **63**, 572) for the rough assay of essence of vanilla:

The vanilla extract is treated with freshly-precipitated lead hydroxide, and to an aliquot part of the filtrate, after dilution, bromine water is added, drop by drop, until the colour of bromine no longer disappears on shaking the liquid. By careful addition of a 1% solution of ferrous sulphate a bluish-green colour is developed, which gradually increases in intensity to a maximum. By comparing this colour with that produced in a solution of known vanillin content, the estimation of the quantity of the vanillin in the extract may be effected.

***iso*-Vanillin,** $C_6H_3(CHO)^1(OH)^3(OCH_3)^4$, is an isomeride of vanillin obtained by heating opianic acid under pressure with dilute hydrochloric acid, and is formed in small quantity, together with vanillin, in many reactions. It forms vitreous prisms (m. p. 115°, b. p. 179°), yielding a vapour which has an odour resembling that of vanilla and anise. *iso*-Vanillin gives no coloration with ferric chloride.

Piperonal. $C_8H_6O_3$; *i. e.*,



Piperonal, or *heliotropin*, as it is commercially named, has the constitution of *methylene-protocatechuic aldehyde.* It was originally produced by the gradual addition of a solution of potassium permanganate to one of potassium piperate obtained by the saponification of piperine, the alkaloid of pepper. The liquid acquires a pleasant odour like that of coumarin, and yields piperonal on distillation.

Piperonal is manufactured from *safrole*, $C_6H_3(C_3H_5)^1(O_2.CH_2)^{3;4}$, a leading constituent of the oils of sassafras and camphor. By the action of sodium hydroxide the safrole is converted into *iso*safrole, which is oxidised with potassium dichromate and sulphuric acid.

Piperonal crystallises in large lustrous prisms or thin plates, m. p. 37°. It has a very pleasant odour, closely resembling that of the heliotrope, and on this account is extensively employed in perfumery under the name of "heliotropin." Piperonal is very sparingly soluble in cold water, but more readily in hot, and dissolves very easily in alcohol and ether. It has the general characters of an aldehyde. Its compound with sodium hydrogen sulphite crystallises in laminæ and is but slightly soluble in water or alcohol. By treatment with oxidising agents or boiling with alcoholic potassium hydroxide piperonal is converted into *piperonylic acid* (page 538), whilst on reduction of its boiling aqueous solution by sodium amalgam it yields *piperonyl alcohol*, $C_6H_3.(O_2:CH_2).CH_2OH$, a sparingly soluble substance, m. p. 51°.

When heated under pressure at 200°, with dilute hydrochloric acid, piperonal is decomposed into protocatechuic aldehyde and finely divided carbon.

In doses of 0.5 to 1.0 grm. piperonal has been employed as an antiseptic and antipyretic of moderate power, but some observers find it to be devoid of physiological action. By far its most important application is in perfumery.

Piperonal is injuriously affected by exposure to a temperature above or approaching its m. p., and is preferably preserved in alcoholic solution. It is liable to the same kinds of adulteration as vanillin, and, in addition, to contain an admixture of vanillin itself.

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GALLIC ACID AND ITS ALLIES

By W. P. DREAPER, O. B. E., F. I. C.

Of the 6 possible compounds having the constitution of trihydroxybenzoic acids, the 3 following isomers are well known:

Gallic acid	Pyrogallol-carboxylic acid	Phloroglucinol-carboxylic acid
$C_6H_2\left\{\begin{array}{l}\mathrm{COOH}^{(1)}\\ \mathrm{OH}^{(3)}\\ \mathrm{OH}^{(4)}\\ \mathrm{OH}^{(5)}\end{array}\right.$	$C_6H_2\left\{\begin{array}{l}\mathrm{COOH}^{(1)}\\ \mathrm{OH}^{(2)}\\ \mathrm{OH}^{(3)}\\ \mathrm{OH}^{(4)}\end{array}\right.$	$C_6H_2\left\{\begin{array}{l}\mathrm{COOH}^{(1)}\\ \mathrm{OH}^{(2)}\\ \mathrm{OH}^{(4)}\\ \mathrm{OH}^{(6)}\end{array}\right.$

Of these compounds, gallic acid is the only one of practical interest.[1]

GALLIC ACID. $C_6H_2(OH)_3.COOH + H_2O$

Gallic acid occurs naturally in the free condition in gall-nuts, tea, sumac, divi-divi, mangoes, pomegranates, and many other plants, and may be obtained artificially by fusing brom-hydroxybenzoic acid or bromo-protocatechuic acid with potassium hydroxide. It is usually prepared, however, by the action of boiling dilute sulphuric acid on ordinary tannic acid (gallotannin), or, as it is frequently termed, gallotannic acid.[2] In this change 1 molecule of gallotannin is hydrolysed taking up a molecule of water, with the formation of 2 molecules of gallic acid.

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[1] PYROGALLOL-CARBOXYLIC ACID is obtained when pyrogallol is heated with potassium hydrogen carbonate (*Ber.*, 1885, **18**, 3205). It decomposes when heated to 195°, but may be sublimed without decomposition in a current of carbon dioxide. The solution gives a violet coloration with ferric chloride.

PHLOROGLUCINOL-CARBOXYLIC ACID is obtained by boiling phloroglucinol with an aqueous solution of potassium carbonate. It decomposes at 100°, or when boiled with water, into phloroglucinol and carbon dioxide.

[2] The tannin extract is introduced, in a crude state, into a lead-lined vacuum pan, together with the necessary quantity of sulphuric acid, and the whole is heated to about 50° to 65° in a vacuum of 500 mm. Nearly the whole of the gallotannic acid is converted into gallic acid, and the concentration is kept up by the reintroduction of spent mother-liquor from the crystallising pans. Under these conditions the brown amorphous products obtained when the operation is conducted in open vessels are no longer formed; and, after the reaction is complete, the liquor can be concentrated until the gallic acid begins to separate by crystallisation. The crude product is in the form of yellow crystals, which furnish a pure, colourless acid on double crystallisation in presence of animal charcoal free from lime.

The change which takes place was for long accepted to be in accordance with the formula of Schiff (*Ann. Chem. Pharm.*, 1873, **162**, 43), according to which gallotannin is an anhydride of digallic acid.

$$\begin{array}{lcl} C_{14}H_{10}O_9 + H_2O & = & 2C_7H_6O_5. \\ \text{Digallic or} & & \text{Gallic acid.} \\ \text{tannic acid.} & & \end{array}$$

The change is much more complicated than this, however, and Nierenstein's formula (*J. Soc. Chem. Ind.*, 1922, **41**, 29T), which represents gallotannin as a glucoside of a polyleucodigalloyl digallic anhydride, is more in keeping with the observed optical properties of gallotannin. (See TANNIN).

As in the case of many other changes of a hydrolytic nature, the same result may be brought about by the action of the natural enzymes in certain mould-fungi.[1] To bring about this change, the powdered galls are moistened with water and exposed to the air for several weeks. The dark-coloured mass is washed with a little cold water and then boiled with more water, which extracts the gallic acid.

Gallic acid occurs in the form of acicular prisms or silky needles, either white or, generally, of a faint buff colour, containing 1 molecule of water of crystallisation. It is odourless, and possesses a faintly acid taste. It loses its water of crystallisation at 100°. (Böttinger states that gallic acid does not become anhydrous below 120°, but this is incorrect).

When heated to a temperature of 210° to 220°, gallic acid melts and then decomposes, with formation of carbon dioxide and *pyrogallol*, $C_6H_3(OH)_3$, which latter substance can be obtained as a sublimate. If the temperature be raised rapidly to 250°, water is given off, in addition to carbon dioxide, and a considerable proportion of a deep-coloured, lustrous substance, which consists chiefly of *metagallic acid*, $C_6H_4O_2$, is left in the retort.

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[1] A. Fernbach (*Compt. rend.*, 1900, **131**, 1214) found that it is the mould-fungi formed in the gallic acid fermentation which bring about the hydrolysis of the tannin by a special ferment, *tannase*. Fernbach isolated this enzyme by cultivating *Aspergillus niger* in Raulin's liquid containing tannin in place of sugar. By precipitation with alcohol, H. Pottevin (*loc. cit.*) obtained tannase as a grey powder, the neutral or acidified solution of which is much more active than the original liquid. It acts most powerfully at 67°, is contained in sumac leaves, and appears to be widely distributed in the vegetable kingdom.

Knudson (*J. Biol. Chem.*, 1913, **14**, 159) has found that solutions of gallotannin are toxic to many mould-fungi, and that the only ones capable of forming in 10 % solutions of gallotannin are *A. flavus*, *A. niger*, *A. oryzæ* and *Penicillum* species.

It has been shown by Mitchell (*Analyst*, 1923, **47**, 7) that the tinctorial value of gallotannin, on treatment with iron salts, is doubled in the course of enzymic hydrolysis. Under certain conditions the enzymic reaction is reversible.

Solvent	Parts of gallic acid dissolved	Solvent	Parts of gallic acid dissolved
Acetone	29.4	Mixed benzene and ethyl acetate (1:1)	0.77
Acetone + 5% water	22.2	Ether (anhydrous)	2.5
Alcohol (absolute)	22.2	Ether (moist)	2.7
Alcohol (90%)	18.[illegible]	Sodium chloride (26.9%)	0.96
Ethyl acetate	8.1	Water (at 12.5°)	0.76

Gallic acid is soluble in about 100 parts of cold or 3 parts of boiling water. The hot solution yields an abundant deposit of crystals of the hydrated acid on cooling. Gallic acid is soluble in 5 parts of 90% alcohol, in 40 parts of ether, and in 12 of glycerol.[1] The figures for solubility of gallic acid according to the U. S. Pharmacopœia, at 25°, are: water 83.7 parts, alcohol 4.14 parts. It is only very slightly soluble in chloroform, benzene, and petroleum spirit.

An aqueous solution of gallic acid has an acid and astringent taste and readily undergoes decomposition. Gallic acid may be extracted from its aqueous solution by agitation with ether or ethyl acetate.

Gallic acid is monobasic, and forms a series of well-defined, but unimportant, crystallisable metallic salts. The gallates of the alkali-metals are stable in the dry state or in acid solution, but in alkaline solution they readily absorb oxygen and become coloured, owing to the formation of *galloflavin*, a yellow dye of the xanthone series. Basic bismuth gallate is described on page 567.

Oxidising agents, such as arsenic acid and iodine, convert gallic acid into *ellagic acid*, which is probably a fluorene derivative.

According to Guignet (*Compt. rend.*, 1891, **113**, 200), when a warm solution of gallic acid is added to a warm mixture of zinc powder and ammonia, it is completely converted into benzoic acid after being heated to 60° for some hours. Benzoic acid is also formed when gallic acid is heated with zinc and dilute sulphuric acid, but in this case the benzoic acid remains undissolved.

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[1] The above table, based on the observations of Rosenheim and Schidrowitz (*Trans.*, 1898, **73**, 882) shows the solubility of gallic acid in 100 parts of various solvents at 15°.

When gallic acid is heated with 5 times its weight of strong sulphuric acid to 100°, it is converted into *rufigallic acid*, $C_{14}H_8O_8$. The liquid first becomes red and next purple, and if then poured into water, nearly pure rufigallic acid is precipitated.[1] If, in the above process, a portion of the gallic acid be replaced by benzoic acid, the product is *anthragallol*, one of the isomeric trihydroxyanthraquinones.

Gallic acid is absorbed by certain organic tissues, such as hide and silk, in the same manner as gallotannin, but far less readily and completely. Vignon (*Compt. rend.*, 1895, **121**, 916) states that ungummed silk absorbs from 7 to 8% of its weight from a 4% solution of gallic acid at a temperature of 80°; but with a bath of 1% strength the absorption is practically *nil*. From a mixed bath of gallotannin and gallic acid the former is preferentially absorbed.

Gallic acid and its derivatives are used to a considerable extent in medicine. Gallic acid is also used as a reducing agent in photography and is a constituent of certain hair-dyes. It is employed as the raw material in the manufacture of pyrogallol.

It has been shown by Mitchell (*Analyst*, 1920, **45**, 255) that on adding hydrogen peroxide to a solution containing gallotannin and ferrous sulphate a black precipitate is immediately produced, whereas gallic acid gives only a dark brown coloration.

Analytical Reactions of Gallic Acid.—An aqueous solution of gallic acid gives the following indications:

On the addition of a solution of ferric chloride a deep blue precipitate is formed, which is soluble in excess of the reagent with green colour. The exact colour of the precipitate is affected by the concentration of the solutions. An excess of gallic acid destroys the colour, and reduces the iron to the ferrous state. A similar change occurs on boiling the liquid.

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[1] RUFIGALLIC ACID, OR RUFIGALLOL, is a *hexahydroxyanthraquinone* of the constitution: $C_{14}H_2O_2(OH)^1(OH)^2(OH)^3(OH)^5(OH)^6(OH)^7$. It forms small, shining, reddish-brown crystals containing $2H_2O$, but becomes anhydrous at 220°, and sublimes at a higher temperature in cinnabar-red prisms. Rufigallic acid dissolves sparingly in hot water, alcohol, and ether. It dissolves with an indigo-blue colour in alkali hydroxide, and gives an indigo-blue precipitate with baryta water. When heated with zinc dust it is reduced to anthracene, $C_{14}H_{10}$.

When pyrogallol is fused with ammonium oxalate it yields ammonium rufigallate, which dissolves in water with red colour, and gives the following reactions: Potassium ferricyanide and potassium dichromate give a dark brown precipitate insoluble in alcohol. Ferric chloride gives no black coloration, and neither sodium nitroprusside nor platinic chloride produce either precipitate or change of colour. On adding a few drops of acetic acid, and then potassium cyanide and mercurous nitrate, a black precipitate is obtained. Alkali hydroxides cause a change to brown but not to black.

In the absence of air, a solution of ferrous sulphate gives a white precipitate with a concentrated solution of gallic acid. With a dilute solution no immediate change occurs, but on exposure to air the liquid becomes bright blue, and deposits a black precipitate without becoming decolorised.

W. H. Ince (*Pharm. J.*, 1887, [3], 17, 461) prepares a neutral solution of ferrous chloride by decomposing cupric chloride by iron filings or wire. He adds this reagent to the solution to be tested for gallic acid, and then gradually adds bromine in excess. Under these conditions, gallic acid gives a faint blue colour on first adding the ferrous chloride, and this is changed to indigo-blue on cautious addition of bromine water or vapour, but the liquid is decolorised on adding excess. Gallotannin gives a red tint changing to green with excess.

On addition of excess of alkali hydroxide to a solution of gallic acid the liquid turns yellow, and ultimately brown and black on exposure to the air, from formation of tanno-melanic acid. The change is accelerated by boiling. On neutralising the black liquid with acetic acid and adding lead acetate, a black precipitate is thrown down. If sodium hydrogen carbonate is used instead of alkali hydroxide, the liquid becomes indigo-blue and deposits a deep bluish-green precipitate, which is turned red by acids.

Lime-water in excess produces a white precipitate with solutions of gallic acid, changing very rapidly to blue.

When ammonium chloride and ammonia are added to a solution of gallic acid no precipitate is formed, but a strong red colour is developed if the solution is strong, or a greenish-coloured ring at the junction of the layers of the liquids is formed if the solution is weak.

A red colour is produced in solutions of gallic acid by chlorine water and ammonia.

With a solution of potassium antimony tartrate, gallic acid yields a white precipitate, even in very dilute solutions, and the filtrate is practically free from gallic acid. The action is prevented by ammonium chloride or acetate. Precipitation as gallate has been proposed as a means of estimating antimony.

Osmium tetroxide gives a violet coloration with solutions of gallic acid; this is an exceedingly sensitive reaction (Mitchell) (cf. TANNINS).

Gallic acid reduces Fehling's solution only slowly and imperfectly, with formation of acetic and pyrotartaric acids and other products (C. Böttinger, *J. Soc. Chem. Ind.*, 1891, **10**, 480). Gallic acid reduces gold and silver solutions (rapidly when hot), and decolorises an acid solution of potassium permanganate, being oxidised to hydrorufigallic acid, $C_{14}H_8O_5$.

In the absence of other reducing agents, gallic acid may be estimated by titration in an acid solution with permanganate, preferably in presence of indigo. If gallotannin is present, it must first be separated by precipitation.

Gelatin or "collin" cannot be used for this purpose owing to the large percentage of gallic acid carried down by the gallotannin coagulum (Dreaper, *Chem. News*, 1904, **90**, 111).

No precipitate (distinction from tannins) is produced with gallic acid by dilute solutions of alkaloids, gelatin, albumin, or starch, but a mixture of gum-arabic and gelatin is precipitated.

In very concentrated solutions gallic acid is precipitated by albumin (Dreaper and Wilson, *J. Soc. Chem. Ind.*, 1906, **25**, 515).

According to Griggi, a 3% solution of potassium cyanide produces, with a 1% solution of gallic acid, a fine ruby-red coloration, which shortly disappears, but can be restored by agitating the liquid. Tannic acid and pyrogallol give a yellowish-red colour when similarly treated. If hydrogen peroxide be added in addition to potassium cyanide, gallic acid still gives a ruby-red coloration; but with gallotannin the colour is yellowish-brown, and with pyrogallol a dirty white turbidity is produced.

The following table exhibits the reactions of gallic acid in juxtaposition with those of gallotannin and pyrogallic acids, to which substances gallic acid presents many points of resemblance:

Reagent	1 % Solution of:		
	Gallotannin	Gallic acid	Pyrogallol
1. Gelatin	White or buff coloured precipitate.	No change, except in presence of gum-arabic.	No change.
2. Ferrous sulphate (free from ferric salt).	No change; white in concentrated solution, darkening on exposure.	No change; white in concentrated solution, darkening on exposure.	White precipitate, changed to blue solution by least trace of ferric salt.
3. Ferric chloride	Blue-black ppt.; colour destroyed by boiling.	Deep blue coloration, destroyed by boiling.	Red colour, turning brown on heating.
4. Ferric acetate	Blue-black ppt.	Purple-black ppt.	Purple-black colour.
5. Ammoniacal ferricyanide.	Deep red coloration destroyed by moderate excess of the reagent.	Vermilion-red coloration, only destroyed by a large excess of reagent.	Intense brown colour.
6. Ammoniacal picric acid.	Reddish.	Red coloration, rapidly changing to fine green.	Reddish colour.
7. Lime-water in excess; or barium chloride and ammonia.	White precipitate, rapidly becoming blue.	White precipitate, very rapidly becoming blue.	No ppt.; immediate purple colour becoming brown in the air.
8. Lead acetate	White ppt. insoluble in acetic acid.	White ppt., soluble in acetic acid.	Slight precipitate.
9. Lead nitrate	White precipitate.	No change.	No change.
10. Tartar emetic	White ppt. insoluble in ammonium chloride.	White ppt. soluble in ammonium chloride.	No change.
11. Bismuth nitrate	White precipitate.	Pale yellow ppt.	Dark greenish ppt.
12. Ammoniacal cupric sulphate.	Precipitate.	No precipitate.	Deep purple-brown coloration.
13. Potassium cyanide.	Yellowish-red.	Ruby-red colour, disappearing on standing, but restored by shaking with air.	Yellowish-red.

With Hübl's iodine solution, gallic acid yields a golden-yellow substance which is readily soluble in water. Tannic acid absorbs less iodine than gallic acid, and gives a yellow, granular product which is nearly insoluble in water.

When a solution of gallic or tannic acid is treated with excess of a 1% solution of iodine in potassium iodide, shaken and tap water or a very dilute solution of a salt with an alkaline reaction added a reddish-violet coloration indicates the presence of gallic acid or gallotannin and is said to distinguish these from tannins which are free from gallic acid. (O. Schewet, *Biochem. Zeitsch.*, 1913, 52, 27)[1].

An ammoniacal solution of potassium ferricyanide produces with gallic acid a very bright red coloration, destroyed only on adding a large excess of the reagent.

An aqueous solution of picric acid to which an excess of ammonia has been previously added produces with gallic acid a red coloration, changing in a few seconds to a beautiful green.

Gallic acid gives a somewhat similar and delicate reaction on addition of a faintly alkaline solution of sodium arsenate, when the surface of the liquid exposed to the air rapidly becomes deep green.

When gallic acid mixed with twice its weight of phenylhydrazine is heated to 100°, or a slightly higher temperature, and then boiled with water, or when the aqueous solutions of the two substances are mixed and boiled, a compound is obtained which dissolves in very dilute sodium hydroxide solution with reddish-yellow, orange, or golden coloration. Tannin, on similar treatment, yields a splendid greenish-blue solution, gradually turning yellow.

Pure gallic acid is optically inactive, whilst gallotannin is active (Rosenheim and Schidrowitz, *Trans.*, 1898, **73**, 880).

ESTIMATION OF GALLIC ACID

W. P. Dreaper (*J. Soc. Chem. Ind.*, 1893, **12**, 412; *Chem. News*, 1904, **90**, 111) has devised a process by which gallic acid can be estimated volumetrically with very fair accuracy. It consists in heating the solution to be tested to about 90°, after adding about 1 grm. of precipitated calcium carbonate, and subsequently cooling to about 25°. In this way the calcium salt of gallic (or tannic) acid is formed before titration. A solution of copper sulphate containing 15 grm. per litre is then added, with agitation, until the precipitate shows a tendency to collect at the bottom of the liquid. A drop of the supernatant liquid is then removed and pressed on a doubled, square inch of filter-paper, to the under leaf of which a drop of solution of potassium ferrocyanide is then applied. If the action is complete, a faint pink coloration will be observed, owing to the formation of cupric ferrocyanide. If no colour is obtained, more copper sulphate must be cautiously added, and the testing of a drop of the liquid repeated. Dreaper found 0.5 grm. of the purest gallic acid obtain able to require 45 c.c. of the standard copper solution for its precipitation.[1]

Gallotannin behaves in the above process exactly like gallic acid, except that 0.5 grm. of the purest specimen obtainable required a different amount of the copper solution for its precipitation. Hence, when a mixture of gallotannin and gallic acids is to be analysed, it is necessary first to separate the former. This is effected by Dreaper by adding to 50 c.c. of the original solution 5 grm. of barium sulphate, followed by 10 c.c. of a solution containing 20 grm. of lead acetate and 60 c.c. glacial acetic acid to the litre, which should be added gradually with constant shaking. The liquid is then filtered through a dry filter-paper, and a small quantity of anhydrous sodium sulphate (0.5 grm.) added. After 5 minutes the lead sulphate is filtered off through another filter-paper and the resulting solution measured, heated with calcium carbonate, and titrated with copper sulphate solution. In all three operations the calcium carbonate used must be pure. The quality "precipitated for analysis" is the best. By this treatment the tannic acid is completely removed, and the gallic acid can be estimated by titrating 40 c.c. of the filtered liquid with copper solution in the manner already described.

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[1] A slight correction should be made for the excess of copper solution needed to yield a visible reaction, as ascertained by a blank experiment.

An approximate estimation of the gallic acid may be made by titrating the filtrate with standard permanganate in presence of sulphuric acid and indigo-carmine.

Another method of separating gallic acid from tannins depends on the insolubility of cupric gallate in water, and its solubility in ammoniacal liquids. The solution is precipitated by excess of cupric acetate, the precipitate washed and digested with a cold solution of ammonium carbonate. The solution, filtered from any insoluble tannate of copper, is evaporated to dryness, the residue moistened with nitric acid, ignited, and the resultant cupric oxide weighed. Its weight, multiplied by 0.9, gives the weight of gallic acid. This method is sometimes applicable to the separation of gallic acid from gallotannic and quercitannic acids, but the copper salts of some varieties of tannin are soluble in ammonium carbonate.

In the absence of gallotannin and other substances which interfere with the action, gallic acid may be estimated by digesting the solution containing it with a known weight of recently ignited oxide of zinc. The insoluble zinc powder is filtered off and washed, dried at 110°, and finally weighed. The increase in weight may be regarded as the amount of gallic acid taken up. Gallic acid may be separated from many varieties of tannin by agitating it in aqueous solution with ether.

The ordinary hide powder process as used in the estimation of tannins is quite useless in the case of gallic acid, as will be seen from figures given by Dreaper (*Chem. News*, 1904, **90**, 111) where results showing errors amounting to between 27.0 and 45.6% are given.

Colorimetric Estimation of Gallic Acid.—An accurate method of estimating gallic acid in the presence of gallotannin has been devised by Mitchell (*Analyst*, 1923, **47**, 1). It is based upon the fact that the presence of a tartrate causes pyrogallol, gallic acid or gallotannin to react immediately with ferrous sulphate, to form a soluble compound which is fairly stable. The colour ranges from reddish violet to bluish violet according to the excess of reagent used, and the reaction is capable of detecting 0.0001 grm. of gallic acid in 100 c.c.

The reagent consists of a solution of 0.1 grm. of ferrous sulphate and 0.5 grm. of Rochelle salt, and under certain conditions appears to be specific for the pyrogallic grouping.

A solution of 0.1 grm. of either pure pyrogallol or pure gallic acid in 100 c.c. of water is used as the standard and the comparison is made in Nessler's tubes with side-tubulures and taps.

In the case of gallic acid or gallotannin 0.1 grm. of the substance is also dissolved in 100 c.c. of water and 1 c.c. of this solution and of the standard solution is added to about 95 c.c. of water in the respective cylinders. 2 c.c. of the reagent are then added to each tube, the solutions made up to 100 c.c. and the colours compared both vertically and horizontally. By running out the darker solution from the tap, and if necessary, further diluting the solutions a series of comparisons is made, and the ratio between the sample and the standard substance established.

In test estimations Mitchell has shown that the colorimetric ratio of pyrogallol, crystalline gallic acid, and anhydrous gallic acid correspond to their molecular weights thus:

		Molecular Weight Ratio
Pyrogallol $C_6H_2(OH)_3.H$	126	1
Crystalline gallic acid $C_6H_2(OH)_3.COOH + H_2O$.	188	1.50
Anhydrous gallic acid $C_6H_2(OH)_3.COOH$........	170	1 36

In each case therefore, the pyrogallic group, $C_6H_2(OH)_3$ is the tinctogenic agent, and the carboxyl group and the water of crystallisation act merely as diluents of that group.

Similarly, in the case of gallotannin a colorimetric ratio, depending upon the proportion of pyrogallic groupings, can be established between it and gallic acid or pyrogallol.

As tannins vary considerably in composition, it is necessary to use a factor suitable to the particular class of substances, but in the case of a particularly pure gallotannin practically free from glucose (cf. Nierenstein, (*Analyst*, 1923, **47**, 5; *Ber.*, 1923, 1876) the factor 2.2 expressed the colorimetric ratio towards gallic acid.

In estimating gallic acid in the presence of gallotannin the two substances are first estimated together colorimetrically, as described, and the results expressed in terms of pure gallic acid or pure pyrogallol.

An aliquot portion of the solution is then treated with a slight excess of powdered quinine hydrochloride. This precipitates the tannin, leaving the gallic acid in solution, and a second estimation is then made with the filtrate. The difference between the results, in terms of gallic acid or pyrogallol, obtained in the two estimations gives the amount of gallic acid present.

For applications of this method to the analysis of different commercial materials containing tannins (see TANNINS, Vol. V).

Esters and Derivatives of Gallic Acid.—A number of derivatives of gallic acid have found application in medicine. The following are the most important of these:

Bismuth Subgallate, brought out under the trade name of "dermatol" is a basic gallate of bismuth of the formula,

$$C_6H_2(OH)_3.COOBi(OH)_2.$$

It forms a soft, bright yellow, tasteless, odourless powder, which reddens litmus-paper, but is almost insoluble in water, alcohol, and ether. It should be wholly soluble in dilute acids and in sodium hydroxide solution, and should give no indication for nitrates with diphenylamine. Bismuth subgallate is a valuable substitute for iodoform, and in doses of 0.25 to 0.5 grm. is employed internally in the treatment of diarrhœa.

The following tests are given in the United States Pharmacopœia.

Bismuth subgallate should yield not less than 52% nor more than 57% of pure bismuth oxide.

An amorphous, bright yellow powder, somewhat variable in chemical composition, without odour or taste, and permanent in the air.

Insoluble in water, alcohol, and ether; readily, with decomposition, in hot hydrochloric, nitric, and sulphuric acids; insoluble in very dilute mineral acids; readily soluble in solutions of the alkali hydroxides, forming a clear yellow-coloured solution, which readily changes to a deep red.

When heated to 120° the salt loses from 5 to 7% of water, and on subsequent heating to redness it at first chars, finally leaving a yellow residue, which is soluble in hydrochloric and nitric acids and is blackened by ammonium sulphide T. S.

Upon thoroughly agitating 0.1 grm. of bismuth subgallate with an excess of hydrogen sulphide T. S., a black precipitate results; on filtering and then boiling the filtrate to remove the dissolved gas the cold filtrate, after the addition of 1 drop of ferric chloride T. S., will assume a blue-black coloration.

If 9.5 grm. of the salt are well shaken with 5 c.c. of alcohol and filtered at once, the filtrate should not turn moistened blue litmus-paper red (absence of free gallic acid).

If 0.5 grm. of bismuth subgallate is well mixed with 5 c.c. of dilute sulphuric acid and 5 c.c. of ferrous sulphide T. S., the mixture filtered and the filtrate cautiously poured, without shaking, over 5 c.c. of sulphuric acid (free from nitrous compounds) contained in a test-tube, no brown ring should form after standing for ten minutes (limit of nitrate).

If 3 grm. of bismuth subgallate are ignited in a porcelain crucible, and, after cooling, nitric acid is cautiously added to the residue, drop by drop, the mixture heated until solution is complete and evaporated to dryness, the residue again ignited and cooled, treated with nitric acid, concentrated to 4 c.c., poured into 100 c.c. of water, the solution filtered, the filtrate evaporated on the water bath to 30 c.c. and again filtered, and this filtrate divided into portions of 5 c.c., then each of these should respond to the test for purity described under *Bismuth subcarbonas*.

The residue resulting from the ignition and subsequent treatment of 2 grm. of the salt, as described below, should not respond to Bettendorf's test for arsenic.

If 1 grm. of bismuth subgallate is thoroughly ignited in a porcelain crucible, and, after cooling, 5 c.c. of nitric acid are added to the residue, drop by drop, the liquid warmed until complete solution has been effected, the solution, upon evaporating to dryness and again igniting, should leave a residue of bismuth oxide weighing not less than 0.52 grm. nor more than 0.57 grm.

Average dose, 0.250 grm. = 250 milligrammes (4 grains).

"Airol," a compound of the formula $C_6H_2(OH)_3.COOBi(OH)I$, possesses both the absorbent properties of dermatol and the antiseptic properties of its iodine. It forms a greenish-grey, odourless, tasteless powder, which loses iodine on exposure to moist air. "*Iodogallicin*" is a methyl-derivative of airol.

"Gallicin," or methyl gallate, $C_6H_2(OH)_3.COO(CH_3)$, is prepared by passing a current of dry hydrogen chloride gas through a solution of gallic acid in methyl alcohol. It forms fine needles or prisms which melt at 202°, and are readily soluble in water and alcohol. It is used as an antiseptic dusting powder and in certain eye diseases.

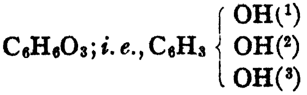
"Bismal."—Gallic acid readily condenses with formaldehyde to form substances typified by *methylene-digallic acid*, or *methylene gallate*, $C_6H_2(OH)_3.CO.O.CH_2.OCO.(OH)_3C_6H_2$. The *bismuth* salt of this compound, said by Merck to be $4C_{15}H_{12}O_{10} + 3Bi(OH)_3$, is the "bismal" of commerce. It forms a bluish-grey, voluminous powder, soluble, with yellow or red colour, in solutions of alkalies and reprecipitated by acids. It is recommended in doses of 0.1 to 0.3 grm. as an internal astringent in chronic diarrhœa (compare *Ber.*, 1898, 31, 259).

"Gallobromol" is a *dibromogallic acid*, $C_6Br_2(OH)_3.COOH$. It is obtained by the direct action of bromine on gallic acid, and forms fine white needles of bitter taste, almost insoluble in cold, but readily soluble in boiling water. It is also dissolved by alcohol and ether. It is a valuable substitute for metallic bromides as a sedative in nervous complaints.

"Gallanol," or *galanilide*, $C_6H_2(OH)_3.CO.NH.C_6H_5$. This substance forms white crystals melting at 205°, soluble in water, alcohol, and ether. It has marked astringent properties and, being less irritant and non-poisonous, is preferred to chrysophanic acid and pyrogallol in the treatment of skin diseases.

Gallacetophenone, $C_6H_2(OH)_3.CO(CH_3)$, has already been described on page 412.

Pyrogallol. Pyrogallic Acid.



$$C_6H_6O_3;\ i.\,e.,\ C_6H_3\begin{cases}OH(^1)\\OH(^2)\\OH(^3)\end{cases}$$

Pyrogallol has the constitution of a trihydroxy-benzene, and hence is isomeric with phloroglucinol and hydroxyquinol. Thus:

	Pyrogallol	Phloroglucinol	Hydroxyquinol
Position of OH-groups in benzene-ring.	1 : 2 : 3	1 : 3 : 5	1 : 2 : 4
M. p., ° . .	131°	218°	140.5°
Coloration with ferric chloride	Red	Dark violet	Greenish-brown

Phloroglucinol is described in Vol. V. Hydroxyquinol has no practical interest.

Pyrogallol is produced when carbon dioxide is split off from gallic acid or from the isomeric pyrogallol-carboxylic acid, in both of which compounds the 3 hydroxyl groups occupy consecutive positions in the benzene nucleus. Pyrogallol is formed when the above-named acids are heated alone, as was first observed by Scheele (1786), but it is better obtained by heating with water to 210°. It may also be prepared by heating a solution of commercial gallotannic acid in glycerin to 200°, diluting with water, and extracting the pyrogallol by agitation with ether.

Pyrogallol may be conveniently obtained by mixing gallic acid with twice its weight of aniline. The mixture at first becomes liquid, and then suddenly solidifies, with rise of temperature. On heating the product to 120° till carbon dioxide is no longer evolved, *aniline pyrogallate* separates out, on cooling, in long needles, melting at 55° to 56°. On treating this compound with cold benzene, pure aniline is dissolved, and pyrogallol remains insoluble. Several organic bases besides aniline effect the same result, but pyridine does not react until heated considerably above its b. p.

Pyrogallol can also be prepared by fusing either of the two para-chlorphenol-disulphonic acids with potassium hydroxide, and it results from the action of fused alkali hydroxide on hæmatoxylin.

Pyrogallol forms white leaflets or thin lustrous needles, having a sp. gr. of 1.463. It melts at 131° to 132° (not at 115° to 118°, as sometimes stated). When cautiously heated above this temperature, pyrogallol can be sublimed without decomposition; but when rapidly heated to 250°, it loses the elements of water and is converted into a more or less indefinite substance termed *metagallic acid,* which forms a black, amorphous mass insoluble in water but soluble in solutions of alkalies.

Pyrogallol dissolves in less than 3 parts of cold water, to form a solution of acid and bitter taste. It is also freely soluble in alcohol and ether, but practically insoluble in absolute chloroform.

Pyrogallol forms salts with bases, but its acidic characters are not very strongly marked, and the salts are very unstable.[1] Pyrogallic acid itself is stable in the dry state, when the atmosphere is free from ammonia, but in moist or ammoniacal air it gradually darkens and turns brown. In aqueous solution this change occurs far more rapidly, and is attended with absorption of oxygen.[2] In the presence of ammonia or fixed alkali, the absorption of oxygen by pyrogallol is extremely rapid, the liquid quickly becoming brown and finally black. This behaviour of an alkaline solution of pyrogallol is employed for the estimation of oxygen in air and other gaseous mixtures, but has been objected to on the ground that the absorption of oxygen is attended with simultaneous evolution of carbonic oxide.[3]

According to M. Berthelot (*Compt. rend.*, 1898, **126**, 1459), the chief products of the oxidation of pyrogallol in presence of potassium or sodium hydroxide are carbon dioxide and about 86% of a dark brown substance soluble in water having the composition $C_{20}H_{20}O_{16}$. A dark red, crystallisable substance, containing $C_{20}H_{20}O_{11}$, soluble in ether and having some of the properties of purpurogallin (from which it differs by $2H_2O$), is formed in the early stages of oxidation; while another substance soluble in ether, and of the probable formula

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[1] *Barium pyrogallate*, $C_6H_3(OH)O_2Ba + 4H_2O$, has been prepared by mixing aqueous pyrogallol with excess of baryta water. It forms colourless needles which rapidly blacken in the air, and are decomposed when boiled with water.

[2] The oxidation of pyrogallol in acid or neutral solutions results in the formation of purpurogallol or purpurogallin, a compound of the formula $C_{20}H_{16}O_9$. It is most readily obtained by treating a solution of 20 parts of pyrogallol in 330 parts of water with a solution of 87 parts of potassium ferricyanide in 330 parts of water. Gas is evolved, the solution loses its deep red colour, and purpurogallin separates, the oxidation being complete in about half an hour. Purpurogallin crystallises from alcohol in brown velvet-like needles, melting at 156°, and volatilising at 200° with partial decomposition. It dissolves with difficulty in water, but readily in alcohol and ether, and is soluble in alkalies to form unstable blue compounds. The sodium salt contains Na_4, and gives with barium chloride an almost insoluble precipitate of the barium compound. In strong sulphuric acid, purpurogallin dissolves to a liquid which gives an intense violet coloration when a trace of nitrous acid or a nitrite is added. The colour is fugitive, but the test is said to be delicate and characteristic (S. C. Hooker, *Ber.*, 1887, 20, 3259).

[3] F. Clowes (*Proc. Chem. Soc*, 1895, p. 200) finds that when the absorption of oxygen is effected by a solution containing 10 grm. of pyrogallol and 24 of potassium hydroxide per 100 c.c., no carbon monoxide is evolved unless the oxygen in the gaseous mixture exceeds 28 %, and in such cases perfectly accurate determinations of oxygen are obtainable if the carbon monoxide evolved is absorbed by cuprous chloride before taking the reading. If the proportion of alkali hydroxide be increased to 120 grm. per 100 c.c., no evolution of carbonic oxide occurs. The question has been further studied by M. P. E. Berthelot (*Compt. rend.*, 1898, **126**, 1066, 1459), who states that in presence of 3 molecules of potassium or sodium hydroxide 1 molecule of pyrogallol absorbs 3 atoms of oxygen, the carbon monoxide evolved being 2.2 % of the volume of oxygen absorbed. With 3 equivalents of barium hydroxide, however, only 1 atom of oxygen is absorbed, and less carbon monoxide is formed. With ammonia the absorption is at first very rapid, but is ultimately very slow, 4 atoms of oxygen being ultimately absorbed. No nitrates are formed, but possibly an azo-compound is produced.

$C_{16}H_{16}O_{12}$, exists in the final products in quantity equal to about 10% of the original pyrogallol.

With lime-water, or calcium chloride and ammonia, in presence of air, pyrogallol gives a fine purple coloration, rapidly changing to brown, but no precipitate is produced. The test is delicate and characteristic.[1]

Pyrogallol rapidly reduces salts of mercury, silver, and gold, with precipitation of the metal and formation of acetic and carbonic acids. Fehling's solution and potassium ferricyanide are also reduced, and potassium permanganate in acid solution is rapidly decolorised with evolution of carbon dioxide.

It yields a purple coloration with osmium tetroxide, and the reaction is capable of detecting 1 part in a million of water. An analogous reaction is given by gallotannin, gallic acid, and catechol, but not by resorcinol or phloroglucinol. (Mitchell, *Analyst*, 1924, **49**, 162.)

With ferrous sulphate, especially if a little ferric salt be present, pyrogallol gives a blue coloration, rapidly changing to green and red; and with ferric chloride it at once gives a red coloration, turning brown on heating the liquid. When a tartrate is also present ferrous sulphate gives a violet coloration. A method for the colorimetric estimation of pyrogallol has been based by Mitchell on this reaction (see p. 566).

The aqueous solution of pyrogallol is turned brown by nitrous acid. The test is very delicate.

Pyrogallol does not precipitate a solution of gelatin.

Pyrogallol might probably be estimated by titration in acid solution with standard permanganate, or perhaps by means of Fehling's solution.

Pyrogallol condenses with formaldehyde to form a product of a deep red colour. It forms several well-defined sulphonic acids, which give crystallisable salts (M. Delage, *Compt. rend.*, 1900, **131**, 450).

When fused with ammonium oxalate, pyrogallol yields ***ammonium rufigallate***.

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[1] For examining the behavior of pyrogallol with lime-water, it is convenient to employ a nitrometer filled with mercury. A few cubic centimetres of the solution to be tested for pyrogallol are first allowed to enter through the tap, and the cup is rinsed with water, which is allowed to enter in its turn. Ammonia is next run in, when a slight brown coloration is usually produced owing to dissolved oxygen. On now allowing lime-water or calcium chloride to enter, a fine but rapidly fading purple colour will be developed, and this will be greatly intensified on admitting air and agitating the tube; in fact, in the entire absence of oxygen, the purple-blue colour would probably not be produced. In the absence of calcium (or barium) compounds only a brown colour is produced on admitting air. Addition of potassium ferricyanide to the ammoniacal liquid produces an immediate dark brown coloration, apparently owing to the formation of the same oxidation-product as is produced by admitting air; but ferricyanide prevents the formation of the blue colour with calcium salts, probably by immediately forming the more highly oxidised brown product.

Pyrogallol possesses well-marked toxic properties, and a case of fatal poisoning by its ingestion is on record (*Pharm. Jour.*, 1896, **2**, 260). The lethal dose is about 0.1 grm. per kilo-grm. of body-weight and the symptoms are similar to those produced by phosphorus-poisoning. Pyrogallol retards the heart's action and alters the appearance of the blood (Gibbs and Hare, *Amer. Chem. Jour.*, 1890, **12**, 365).

Ethers and Esters of Pyrogallol

Some of the pyrogallyl esters are prepared on a small scale for medicinal purposes.

Pyrogallyl monacetate, $(OH)_2(O.C_2H_3O_2)$, is known under the name of "*Eugallol.*" It is very soluble in water, but is of too irritating a nature to be used in ordinary dermatological practice. It is of a syrupy consistence and easily soluble in acetone. When a very energetic action on a limited portion of the skin is required, this compound has been found very useful, as it can easily be applied as a solution in acetone, which rapidly evaporates and leaves the eugallol on the desired place. The commercial "Eugallol" contains 33% of acetone. *Pyrogallol triacetate* is a white powder insoluble in water, and is known as "*Lenigallol.*" It has been very successfully employed in cases of psoriasis. The *disalicylate* is known as "saligallol," and is sometimes employed in similar cases.

Pyrogallol dimethyl ether, $C_6H_3(OH).(OCH_3)_2$, and its homologues occur in the less volatile fractions of beechwood-tar. They owe their chief interest to the remarkable series of colouring matters originally prepared from them by Runge.

By condensing pyrogallol-dimethyl ether with tiglic aldehyde, Doebner has obtained an artificial resin closely resembling the natural products. When guaiacol is condensed in conjunction with dimethyl gallate, the resin obtained is isomeric with *guaiaconic acid*, one of the constituents of guaiacum-resin; Doebner's results support the view that the natural resins are in many cases condensation products of phenols with aldehydes.

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(See also section on *Tannins.*)

PHTHALIC ACID AND THE PHTHALEINS

By W. A. DAVIS, B. Sc., A. C. G. I.

PHTHALIC ACIDS

Benzenedicarboxylic Acids, $C_6H_4(CO_2H)_2$

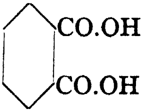
Three isomeric acids of the above composition are known, differing from each other in their properties and structure with the relative positions of the carboxyl groups in the benzene nucleus. Thus, on oxidation with dilute nitric acid or an alkaline solution of potassium permanganate, the 3 isomeric xylenes yield the corresponding phthalic acids. These may, in fact, be regarded as the final products of the limited oxidation of the great majority of benzene derivatives containing 2 side-chains. Hence the differentiation of the phthalic acids affords, in this as in many other cases, a valuable means of distinguishing between allied or isomeric compounds of the aromatic series, and of studying their constitution. The formation of phthalic acid, for example, by the oxidation of naphthalene affords most valuable evidence of the constitution of that hydrocarbon.

The following table exhibits the leading points of difference between the isomeric phthalic acids:

	Orthophthalic or ordinary phthalic acid	Metaphthalic or isophthalic acid	Paraphthalic or terephthalic acid
Formula	$C_6H_4\begin{cases}(1)\ CO.OH\\(2)\ CO.OH\end{cases}$	$C_6H_4\begin{cases}(1)\ CO.OH\\(3)\ CO.OH\end{cases}$	$C_6H_4\begin{cases}(1)\ CO.OH\\(4)\ CO.OH\end{cases}$
Chief sources and modes of formation.	Oxidation of ortho-xylene, alizarin, purpurin, benzene, naphthalene, and naphthalene tetrachloride.	Oxidation of meta-xylene and colophony.	Oxidation of para-xylene, *p*-toluidine, turpentine oil, cymene, cumin oil, eucalyptus oil, etc.
Crystalline form	Monoclinic prisms or nacreous laminæ.	Slender hair-like needles.	Amorphous or crystalline powder.

	Orthophthalic or ordinary phthalic acid	Metaphthalic or isophthalic acid	Paraphthalic or terephthalic acid
M. p.	213° when rapidly heated, giving the anhydride.	Above 300°.	Sublimes without melting.
Solubility in water	Cold, 1 in 180 parts; boiling, more easily soluble (1: 6).	Cold, 1 in 7,800; boiling, 1 in 460 parts.	Cold, very slight; boiling, sparingly.
Solubility in alcohol	1 in 10 parts.	Readily.	Very slight.
Solubility in ether	1 in 146 at 15°.	....	Insoluble.
Action of chromic acid mixture.	Completely oxidised to water and CO_2.	Not affected.	Not affected.
Barium salt	Small scales or silky needles, only slightly soluble in hot water.	Crystallises in readily soluble needles, containing $6H_2O$.	White granular powder or concentrically arranged tablets containing $4H_2O$, soluble in 350 parts of cold water.
Silver salt	Crystalline and moderately soluble; detonates when rapidly heated.	Amorphous precipitate; forms Pharaoh's serpents on heating.	Amorphous precipitate, blackening in the light.
Dimethylester, $C_6H_4(CO_2Me)_2$.	Liquid, b. p. 282°.	Solid, m. p. 64°.	Solid, m. p. 140°.

ORTHO-PHTHALIC ACID,



Ordinary phthalic acid was formerly manufactured on the large scale mainly by converting naphthalene into the tetrachloride, and heating this with 5 to 6 parts of nitric acid of sp. gr. 1.36, till entirely dissolved, when the excess of nitric acid was expelled, and the phthalic acid crystallised out on cooling. It may be purified by re-crystallisation from hot water. The yield by this process is about 30% of the naphthalene used. Phthalic acid may also be obtained by treating naphthalene directly with nitric acid of 1.15 sp. gr., but only about 40% of the theoretical yield is obtained.

According to H. Luddens (*J. Soc. Chem. Ind.*, 1891, **10**, 758), the greater part of the phthalic acid employed in the manufacture of eosin and other phthalein dyes was prepared by the direct oxidation of naphthalene by chromic acid mixture (*sodium* dichromate and sulphuric acid), notwithstanding the general impression that phthalic acid is destroyed by this reagent. This has, however, now been largely superseded by the Badische Anilin-und-Sodafabrik process by which the phthalic acid used in the production of synthetic indigo, is manufactured. This consists in heating naphthalene with fuming sulphuric acid at a temperature of 300° in presence of mercury sulphate, mercury, or its oxides, which act catalytically (English Patent, 18,221, 1896).

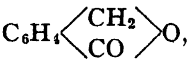
Gibbs and Conover, U. S. Pat's 1,284,888 and 1,285,117 discovered that naphthalene could be oxidized in the vapor phase to phthalic acid by passing the hot vapors over a catalyst containing vanadium pentoxide. This process has been operated by at least three companies in the United States, and a considerable proportion of the american product is made by this general type process.[1]

According to Lossen, the m. p. of phthalic acid is 184°, while Ador states that the crystals melt at 213° and the powder at 203°. These different results depend on the rapidity with which the acid is heated, as a small quantity of the anhydride is formed which lowers the m. p. of the rest of the material. Graebe (*Ber.*, 1896, **29**, 2806) gives the m. p. as about 195°. Neither iso- nor tere-phthalic acid forms an anhydride.

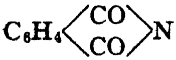
Phthalic acid is readily extracted from aqueous liquids by agitation with ether or benzene, but is insoluble in chloroform (distinction from benzoic acid).

When heated to 330° with a single equivalent of lime, phthalic acid yields calcium benzoate and carbonate: $2C_8H_6O_4 + 2CaO = Ca(C_7H_5O_2)_2 + CaCO_3 + H_2O$. When heated with a larger proportion of lime or other strong base, phthalic acid yields a carbonate and benzene: $C_8H_6O_4 + 2CaO = 2CaCO_3 + C_6H_6$.

By treatment with fuming nitric acid, phthalic acid is converted into nitrophthalic acid, $C_8H_5(NO_2)O_4$, but by strong chromic acid mixture it is completely oxidised.

By treatment with zinc and acetic acid, phthalic acid is converted into phthalide,  $C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O$, diphthalyl, $C_{16}H_8O_4$, being also formed.

When reduced with sodium amalgam phthalic acid gives different *hydrophthalic acids* according to the conditions employed. These reduced acids are of considerable stereochemical interest (see Baeyer's researches, *Annalen*, Vols. **245**, **251**, **258**, **266**, **269**).

When distilled with aniline, phthalic acid is converted into phenylphthalimide or *phthalanil*,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N\,Ph$, a substance which crystallises from alcohol in needles melting at 205°, but volatile at a lower temperature. Phthalanil has been recommended as a febrifuge.

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[1] Amer. Editors.

Besides the extensive employment of its anhydride in the production of dyes, phthalic acid itself has found valuable application as a means of separating certain of the alcoholic constituents of essential oils in a state of purity. Thus the acid phthalates of these substances are readily prepared and may be differentiated by their solubilities and other characters.

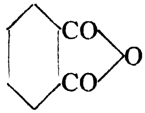
By the prolonged heating of a mixture of glycerin with phthalic anhydride or phthalic acid, and distilling the product *in vacuo*, Watson Smith (*J. Soc. Chem. Ind.*, 1901, **20**, 1075) obtained *diglyceryl triphthalate* as a transparent vitreous solid, which softens on heating and may be employed as a cement for glass and porcelain. It is insoluble in almost all solvents, but dissolves to a slight extent in glycerin and acetone.

On heating glyceryl phthalate with resorcinol, *fluorescein* is formed. This is a useful test for the presence of combined phthalic acid.

Qualitative Test.—When phthalic acid (or its anhydride) is fused in a test-tube with a little resorcinol and the product is dissolved in very dilute sodium hydroxide solution, a strongly fluorescent solution (fluorescein) is obtained.

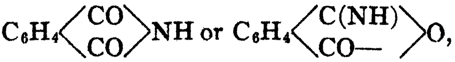
PHTHALIC ANHYDRIDE

Phthalic Oxide,



Phthalic anhydride is prepared by heating phthalic acid to about 200° in a current of air or carbon dioxide, when the anhydride sublimes in long, white, pliant, rhombic needles. It melts at 128° and 130° (Gibbs, *J. Ind. Eng. Chem.*, 1920, **12**, 1017),[1] and boils at 284.5° (thermometer in vapour, Graebe, *Ber.*, 1884, **17**, 1176). Lossen (*Annalen*, 1867, **144**, 76) gives the b. p. 276°. It is only very slightly soluble in cold, but more readily in hot water, and is reconverted into phthalic acid by prolonged boiling with water, more readily in the presence of alkalies.

Gaseous ammonia combines readily with phthalic anhydride on warming, forming *phthalimide*,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NH \text{ or } C_6H_4{<}\begin{matrix}C(NH)\\CO—\end{matrix}{>}O,$$

which melts at 233.5° (Corr.) (Graebe).

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[1] In the *J. Ind. Eng. Chem.*, 1920, 1921 will be found considerable discussion of this m. p. figure, patent litigation being involved. Amer. Ed.

Phthalic anhydride is manufactured extensively for the preparation of the class of colouring-matters known as *phthaleins*, of which the various eosins and rhodamines are examples. It is also used in the manufacture of synthetic indigotin.

COMMERCIAL "PHTHALIC ACID"

Commercial "phthalic acid" is the anhydride, and forms beautiful long, flat needles, obtained by a process of sublimation. A good commercial article should form magnificient flat needles, melt at 128°, be completely soluble in benzene, and volatilise completely at a gentle heat.

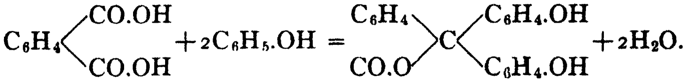
Tests for Impurities.—1 grm. of phthalic acid should on heating leave behind no weighable residue. A solution of 1 grm. of phthalic acid in 25 c.c. of boiling water should only give the very faintest opalescence with silver nitrate (absence of hydrochloric acid). The following test is given by Messner in Lunge's *Chem. Tech. Unt. Meth.*, Vol. 3, 5th Ed. for chlorine compounds (this and the preceding test are of most importance in the case of phthalic acid prepared from naphthalene by means of the tetrachloride). 0.5 grm. of phthalic acid is mixed with 1 grm. of calcium carbonate, free from chlorine, moistened with water, dried and ignited. The residue is dissolved in nitric acid and water so as to give a volume of 20 c.c., and the solution tested with silver nitrate. There should be only a faint opalescence. To test for benzoic acid in phthalic acid, the latter (1 grm.) is shaken with 20 c.c. of benzene and the solution filtered. On evaporating the benzene no residue should remain. As phthalic anhydride is soluble in benzene, before applying this test it must be converted into the acid by dissolving in hot water, evaporating and drying at 100°.

Quantitative Estimation.—1 grm. of the acid or anhydride is dissolved in 20 c.c. of N-sodium hydroxide solution and the solution titrated back with N-hydrochloric acid. 1 c.c. of N-alkali = 0.0830 grm. phthalic acid or 0.0740 grm. of the anhydride.

For the estimation of phthalic acid in the anhydride K. P. Monroe (*J. Ind. Eng. Chem.*, 1919, **11**, 1116) gives the following process due to Adams. 0.5 grm. is dissolved in 50 c.c. of acetone and a few drops of Bromophenol Blue indicator added and the solution titrated with N/10 normal potassium phthalate solution in 80% alcohol. In the presence of phthalic acid the end point is reached when sufficient phthalate has been added to produce the acid phthalate and a further addition causes the colour to change to indigo blue.

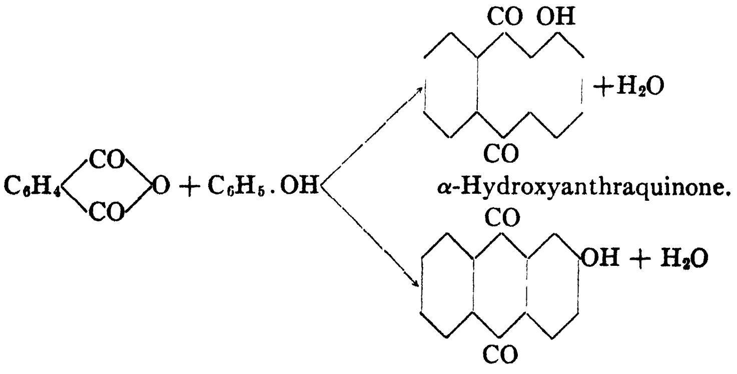
PHTHALEINS

The phthaleins are compounds produced by the action of phthalic acid or anhydride on phenols, with elimination of water. Thus, at a moderate temperature, 2 molecules of ordinary phenol act upon one of phthalic acid or anhydride to form *phenolphthalein:*



$$C_6H_4\left<\begin{matrix}CO.OH\\ CO.OH\end{matrix}\right. + 2C_6H_5.OH = \left.\begin{matrix}C_6H_4\\ CO.O\end{matrix}\right>C\left<\begin{matrix}C_6H_4.OH\\ C_6H_4.OH\end{matrix}\right. + 2H_2O.$$

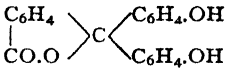
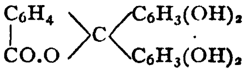
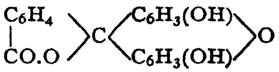
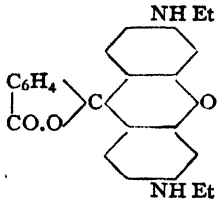
The action is generally carried out by condensing the 2 substances in presence of conc. sulphuric acid or tin chloride at 115 to 120°. When equimolecular proportions of phenol and phthalic anhydride are heated with sulphuric acid at higher temperatures (above 150°) a different action occurs, the two isomeric *hydroxyanthraquinones* being formed.



β-Hydroxyanthraquinone.

Similarly, when resorcinol, $C_6H_4(OH)_2$, is heated with excess of phthalic anhydride to about 200° for half an hour, the mixture acquires a yellowish-red colour, and contains *fluorescein*, $C_{20}H_{12}O_5$, the anhydride of *resorcinol-phthalein*. The melt dissolves in dilute sodium hydroxide or ammonia with dark red colour, the solution changing on dilution to reddish-yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colourless by transmitted light. On acidifying the solution and agitating with ether, the fluorescein is taken up, and will be again dissolved on agitating the ethereal solution with caustic soda. If phloroglucinol be substituted for resorcinol a yellow liquid is obtained, while pyrogallol yields a blue; but neither is fluorescent. The blue colour due to pyrogallol may be destroyed by cautious addition of permanganate, which acts only slowly on fluorescein. *Catecholphthalein*, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in sodium hydroxide solution with a fine blue colour.[1] *Quinolphthalein* is prepared in a similar manner from quinol.

As a class, the phthaleins are weak acid substances which are nearly insoluble in water, but soluble in alcohol and readily so in ether. Their salts with the alkali metals are soluble and strongly coloured. By the action of nascent hydrogen, the phthaleins are reduced to the corresponding *phthalins* (see below) which are colourless substances capable of absorbing oxygen from the air and regenerating the phthaleins.

Commercial name	Chemical name or nature	Formula (lactone form)
Phenolphthalein (Purgen, laxoin, laxitol, phenolax)	Phenolphthalein	 $\begin{array}{l}C_6H_4\\ \vert\\ CO.O\end{array}>C<\begin{array}{l}C_6H_4.OH\\ C_6H_4.OH\end{array}$
Resorcinolphthalein	Resorcinolphthalein	 $\begin{array}{l}C_6H_4\\ \vert\\ CO.O\end{array}>C<\begin{array}{l}C_6H_3(OH)_2\\ C_6H_3(OH)_2\end{array}$
Fluorescein	Anhydride of resorcinolphthalein	 $\begin{array}{l}C_6H_4\\ \vert\\ CO.O\end{array}>C<\begin{array}{l}C_6H_3(OH)\\ C_6H_3(OH)\end{array}>O$
Eosin	Tetrabromofluorescein	
Erythrosin	Tetraiodoeosin	
Rhodamines	Various phthaleins derived from *m*-aminophenol.	*e. g.,*  Colourless form of diethylrhodamine.

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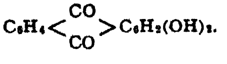
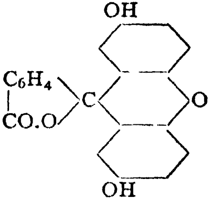
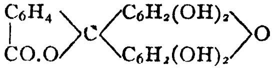
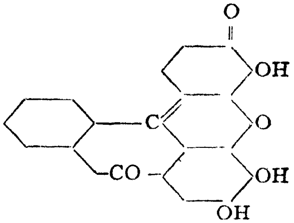
[1] In the 3rd edition (Vol. 2, part iii, p. 131), quinol-phthalein and quinizarin were spoken of as being identical; quinizarin is 1:4-dihydroxyanthraquinone,

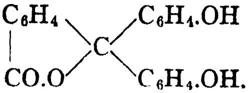


$$C_6H_4<\begin{array}{c}CO\\ CO\end{array}>C_6H_2(OH)_2.$$

Commercial name	Chemical name or nature	(Formula lactone form)
Quinolphthalein.....	Quinolphthalein.......	
Gallein............	Pyrogallolphthalein anhydride, $C_{20}H_{12}O_7$.	
Cœrulein...........	Double anhydride of pyrogallolphthalein, $C_{20}H_{10}O_6$.	

The above table shows the composition of some of the principal phthaleins, the formula given representing in each case the structure of the colourless lactone form. The eosins, rhodamines, etc., will be dealt with more fully in Vol. VI. Phenolphthalein, gallein and cœrulein are described below.

PHENOLPHTHALEIN, $C_{20}H_{14}O_4$ =



$$\begin{array}{l}C_6H_4\\ |\\ CO.O\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_4.OH\\ \\ C_6H_4.OH.\end{array}$$

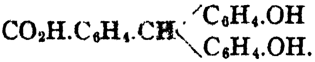
Preparation and Properties.—Phenolphthalein is prepared by heating together 5 parts of phthalic anhydride, 10 of phenol, and 4 of concentrated sulphuric acid during 10 hours at 120°.

The product is boiled with water, and the residue dissolved in dilute sodium hydroxide. On filtering the liquid, the anhydride remains behind, while the phenolphthalein itself is precipitated on treating the filtrate with acetic acid and a little hydrochloric acid. It may be purified by dissolving in alcohol, boiling with animal charcoal, and reprecipitating by diluting the liquid with boiling water.

Phenolphthalein on crystallisation from alcohol is obtained in colourless crusts, melting at 250°. It is only slightly soluble in water, but is readily dissolved by alcohol and ether. In solutions of alkali-metal hydroxides and carbonates, it dissolves with deep red colour.

Silver nitrate gives a violet precipitate with a solution of phenolphthalein.

On treatment with sodium hydroxide and zinc dust, phenolphthalein takes up 2 atoms of hydrogen, and is reduced to *phthalin*, or *p-dihydroxy-triphenyl methane-o-carboxylic acid*,

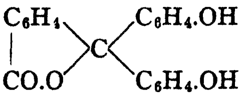


$$\mathrm{CO_2H.C_6H_4.CH}\Big\langle\begin{matrix}\mathrm{C_6H_4.OH}\\ \mathrm{C_6H_4.OH.}\end{matrix}$$

This substance forms small needles melting at 225°, and is soluble in alkali hydroxides without colour, but its alkaline solution is immediately turned red by adding potassium ferricyanide, owing to the formation of phenolphthalein.

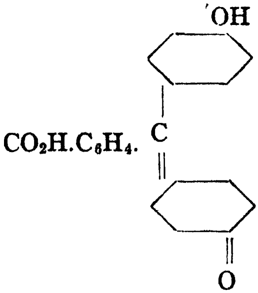
Phenolphthalein is not used in dyeing. It finds some use in medicine as a laxative, in doses from 1 to 5 grains (0.05 to 0.3 grm.), and is sold under the names *purgen*, *laxoin*, *laxatol*, *laxen* and *phenolax*. Its chief interest, however, is as an indicator of neutrality, for which application it is invaluable.

Structure of Phenolphthalein and Its Salts



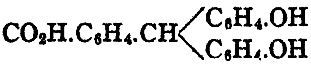
Free phenolphthalein (colourless)

I



Phenolphthalein in its salts (quinonoid form)

II



$$\mathrm{CO_2H.C_6H_4.CH}\Big\langle\begin{matrix}\mathrm{C_6H_4.OH}\\ \mathrm{C_6H_4.OH}\end{matrix}$$

Phthalin

III

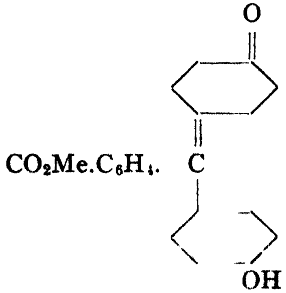
Formula I represents the colourless form of phenolphthalein as a lactonic derivative of triphenylcarbinol. Its close relationship with the triphenylmethane series is clear from its yielding phenolphthalin (Formula III) on reduction. While there is little doubt that formula I correctly respresents the structure of free phenolphthalein, there has been much discussion as to the constitution of its salts, which differ from the colourless parent substance in being highly coloured. Ostwald suggested in explanation of the striking fact that the salts are coloured, that, whereas phenolphthalein itself is not dissociated in solution, existing in the molecular state, the salts are dissociated and that the negative ion is the source of the colour. In aqueous solution the dissociation,

$$\text{Phenolphthalein} \rightleftarrows C_{20}H_{13}O_4{}' \text{ (red)} + H^{\cdot}$$

is so slight that the solution appears practically colourless. If a strong base, such as potassium hydroxide, be added, the OH'-ions of the base combine with the $H^{\cdot}$-ions of the indicator to form water and the equilibrium expressed by the equation given above is destroyed. More phenolphthalein then dissociates until sufficient $C_{20}H_{13}O_4{}'$-ions have been formed to produce a red coloration.

This explanation, although plausible, fails to explain the real difficulty, namely, why the colourless acid should have a coloured ion, and is weakened in value by the fact that the evidence for the existence of a common coloured ion even in the case of solutions of different salts of the same metal (for example, copper) is by no means conclusive. (For a discussion of this point in full see Kayser's *Handbuch der Spektroskopie.*) The theory of Ostwald seems, indeed, no longer tenable in view of the work of Green and King (*Ber.*, 1906, **39**, 2365; 1907, **40**, 3724. *J. Soc. Chem. Ind.*, 1908, **27**, 3 and 638. Compare R. Meyer, *Ber.*, 1907, **40**, 3603; 1908, **41**, 2446). Instead, the theory originally advanced by Nietzki, that a change of structure occurs in alkaline solution and that the salts of phenolphthalein are derived from the quinonoid form shown in formula II, appears more correct, harmonising as it does with modern views as to the origin of colour. The main fact on which the proof of

Green and King depends is, that it was found possible to prepare coloured *esters* of phenolphthalein, of the type



(Phenolphthalein methyl ester.) Coloured.

Previously all attempts to prepare esters had given merely the colourless lactone *ethers*.

Phenolphthalein as an Indicator.—In the early editions a somewhat general discussion of indicators was included under the heading "Phenolphthalein." In view of the fact that this subject is now dealt with fully in several works on general analytical chemistry (for example, in Lunge's "Technical Methods of Chemical Analysis;" Sutton's "Volumetric Analysis") and in special treatises (see especially *Determination of Hydrogen Ions*, by W. Mansfield Clarke, Baltimore, Williams and Wilkins; *Theory and Use of Indicators*, by E. B. R. Prideaux, London, Constable & Co.) the subject will here be considered only briefly.

According to Ostwald's theory, already referred to, indicators are substances which possess a coloured ion. In the case of phenolphthalein the action supposed to occur in the presence of a trace of alkali has already been discussed. The colourless phenolphthalein is supposed to be a weak acid which is practically undissociated in solution. In presence of a trace of alkali (OH'-ions) red negative ions, $C_{20}H_{13}O_4'$, are liberated. The objections to this view have already been referred to. In the case of methyl-orange, a fairly strong acid (methyl-orange is the sodium salt of dimethylaminobenzenesulphonic acid), the "molecule" is assumed to be red and the negative ion yellow. The colour of the aqueous solution is a mixture of the two colours. The addition of a base intensifies the yellow colour by increasing the number of negative ions, owing to the union of the OH'-ions with the $H^{\cdot}$-ions of the indicator. When an acid is present the added H·-ions diminish the ionisation of the indicator and thus increase the red colour of the acid molecule. Owing to the relatively strong acid character of methyl-orange, with weak acids the number of H·-ions is too small to produce a visible change of colour until a large excess of acid has been added. For weak acids, therefore, methyl-orange is not a suitable indicator: carbonic acid and hydrogen sulphide do not show an acid reaction with this indicator. On the other hand, in titrating weak bases the strong acid character of methyl-orange makes it very suitable for use. In the case of litmus, the ionic theory gives an explanation similar to that adopted in the case of methyl-orange. The molecule of the litmus acid (azolitmic acid) is supposed to be red and the anion of the alkali salt to be blue. The colour of the aqueous solution of the indicator is a mixed shade intermediate between the two, owing to the dissociation being only slight. As the strength of the litmus acid is supposed to be intermediate between that of the acids of phenolphthalein (very weak) and methyl-orange (relatively strong), the properties of litmus as an indicator are intermediate between those of these two substances.

The alternative theory of indicators assumes that in the case of indicators the free acid of the indicator has one colour (in the case of phenolphthalein it is colourless) and the salt of the acid another. The case of the colourless phenolphthalein is slightly abnormal because in the formation of the coloured salt a change of structure (to the quinonoid form) occurs. With methyl-orange, however, the case is simpler, the acid being red and the alkali salts yellow. With indicators, such as *p*-nitrophenol, a similar very great difference exists between the colour of the free acid and that of the alkali salts: a change of structure has also been assumed to occur here.

Whatever theory of indicators be adopted, the suitability of a certain indicator for titrating a given acid or base depends primarily on the "strength"[1] of the acid titrated relatively to that of the acid of the indicator.

The different behaviour of various indicators was explained from this point of view (*Ann. Chim. Ph.*, 1885, [vi], **6**, 506) by Berthelot, who pointed out that an acid which can be accurately titrated with methyl-orange, a relatively strong acid, is one of which the heat-formation exceeds 10.2 calories. Phenolphthalein, on the other hand, which is a very feeble acid, enables any acid to be titrated the heat formation of the potassium salt of which exceeds 6 to 7 calories. With Poirrier's soluble blue still weaker acids can be titrated, but the lower limit of its applicability has not been ascertained, and its indications are in many cases disturbed by dissociation.[1]

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[1] This word is used here in its modern chemical sense, which must not be confused with the *concentration* of the acid.

R. T. Thomson investigated the general behaviour of indicators of neutrality in a very complete manner, and arranged the various indicators in 3 groups,[2] to which Allen added *Poirrier's soluble blue*, CLB, as a fourth, thus:

(A) Methyl-orange group	(B) Litmus group	(C) Phenolphthalein group	(D) Poirrier's soluble blue
Methyl-orange	Litmus	Phenolphthalein	Soluble blue, CLB.
Cochineal	Phenacetolin	Turmeric	
Congo-red		Rosolic acid	
Lacmoid			
Iodeosin			
Dimethyl-amino-azobenzene.			

Broadly, the indicators of the methyl-orange group do not react with any but acids of strong affinity, but are sensitive to bases of feeble affinities, such as are many alkaloids. Litmus is often an uncertain indicator of neutrality, as the point at which the change of colour occurs does not in all cases correspond sharply with the formation of any definite salt. Phenolphthalein is a very delicate and sensitive indicator for the strongest as well as for most very feeble acids.

When intended for use as an indicator, phenolphthalein should be employed as a 1% solution in alcohol. A few drops of this solution, which keeps perfectly, should be added to the liquid to be titrated. The alkali employed may be potassium or sodium hydroxide, but it is important that it should be free from carbonate. Hence barium hydroxide is to be preferred in many cases, since the insolubility of barium carbonate in water ensures the freedom of the solution from that compound. The formation of an insoluble barium salt (*e. g.*, sulphate, oxalate, tartrate) in the liquid is rather an advantage than otherwise, as the pink colouration which marks the completion of the titration is observed with greater facility against the white precipitate than against white porcelain or other external background.

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[1] R. Engel states that about 85 % of the hydrogen of H_3PO_4 and H_3AsO_4 is indicated by Poirrier's blue; while concentrated solutions of KBO_2, K_2PHO_3, K_2PHO_2, KCN, and K_2CO_3 were found to be approximately neutral. Phenol and chloral behave as monobasic acids and resorcinol as a dibasic acid, and all three can be accurately titrated with Poirrier's blue.

[2] For details of the behaviour of these various indicators, Allen's paper on "Neutrality" should be consulted (*Analyst*, 17, 186, 215; and *Pharm. Journ.* [iii], 22, 752, 772). See also G. H. A. Clowes, *Amer. J. Pharm.*, 1904, page 453; Cohn's *Treatise on Indicators and Test-papers;* Glaser's monograph (Wiesbaden, 1901); the article by R. Engel, in Moissan's *Traité de Chimic Minérale*, 1904, 3, p. 494, and the works already cited.

Ammonia is not a suitable alkali for use in conjunction with phenolphthalein. Owing to the formation of *phenol-diiminophthalein*, $C_{20}H_{16}N_2O_2$, a substance giving a colourless solution with alkalies, the results in presence of ammonia are erratic. An approximation to the truth can be obtained by operating at as low a temperature as possible, and employing a large amount of the indicator, but the results are less satisfactory than those readily obtainable by the use of other indicators (see J. H. Long, *Amer. Chem.*, 1889, **11**, 84; *Analyst*, 1890, **15**, 38, 52).

With the aid of phenolphthalein, the great majority of acids can be accurately titrated in aqueous solution. The end of the change is well defined, especially when the titration is from acid indication to alkaline.

Phenolphthalein is particularly valuable for the titration of comparatively feeble acids, the soluble normal salts of which exhibit an alkaline reaction to litmus. In the majority of cases, the point of neutrality with phenolphthalein is reached when sufficient alkali has been added to replace all the basic hydrogen of the acid, but in other cases the neutral point is attained when ½ or ⅔ of this amount of alkali has been added.

Such feeble acids as carbonic and sulphydric can be titrated with phenolphthalein, the point of neutrality in cold solutions being indicated by the formation of the compounds $NaHCO_3$ and NaHS, respectively. On the other hand, aqueous solutions of silicic and boric acids are wholly indifferent to phenolphthalein, so that the whole of the base present as a silicate or borate is indicated on titration with a mineral acid. In presence, however, of a sufficient proportion of glycerol (not less than 30%) R. T. Thomson made the valuable observation that boric acid can be titrated by means of phenolphthalein, the salt $NaBO_2$ being neutral to that indicator under these conditions.

An important advantage possessed by phenolphthalein is that it reacts perfectly in alcoholic solution, and hence allows of the accurate titration of many insoluble or sparingly soluble organic acids, including benzoic, salicylic, palmitic, stearic, oleic, ricinoleic,[1] the acids of colophony, etc.

In many cases (as in the estimation of benzoic acid in paregoric) phenolphthalein may be conveniently employed with an ethereal solution of the acid to be titrated.

Although phenol and other substances containing an OH group have many of the properties of acids, they do not indicate this character to phenolphthalein. This is true of morphine, the molecule of which contains a hydroxyl group having a phenolic function, which enables it to form compounds with the alkalies, and is the cause of its solubility in solutions of alkali hydroxides and lime-water.

In the table given below, which has been enlarged from one compiled by R. T. Thomson (*J. Soc. Chem. Ind.*, 1887, **6**, 198), the figures represent the number of atoms of basic hydrogen displaced by sodium or potassium in the form of alkali hydroxide, when a compound is formed showing neutrality to the indicator in question. Thus when methyl-orange is used in the titration of sulphurous acid the neutral point is reached when sodium hydroxide has been added in quantity sufficient to form the compound $NaHSO_3$; but when phenolphthalein is used, the point of neutrality corresponds to the salt Na_2SO_3. Similarly, NaH_2PO_4 is neutral to methyl-orange, Na_2HPO_4 to phenolphthalein, and Na_3PO_4 to Poirrier's blue.

While phenolphthalein is a delicate indicator even for feeble acids, it is absolutely indifferent to the great majority of organic bases, including even aniline and pyridine. The mydriatic alkaloids (atropine, homatropine, hyoscine, and hyoscyamine) form notable exceptions, the aqueous solutions of the free bases strongly reddening phenolphthalein. This property, however, does not exist in alcoholic solution, a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenolphthalein. According to E. Leger, cicutine (from *Cicuta virosa*) and codeine are also exceptions to the general rule of indifference of the alkaloids to phenolphthalein, and P. C. Plugge states that coniine and nicotine also exhibit an alkaline indication. As a consequence of the indifference of most alkaloids to phenolphthalein, their salts react with this indicator as if the acids

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[1] In the case of the higher fatty acids, titration in alcoholic solution is necessary not only because the acids themselves are insoluble in water, but also owing to the fact that water effects partial decomposition of their alkali-metal salts (soaps).

BASICITY OF ACIDS AS SHOWN BY DIFFERENT INDICATORS WHEN TITRATED IN AQUEOUS SOLUTION WITH FIXED ALKALI HYDROXIDE

Acid		Methyl-orange	Phenol-phthalein		Litmus		Poirier's blue
Name	Formula	Cold	Cold	Boiling	Cold	Boiling	Cold
Hydrochloric	HCl[1]	1	1	1	1	1	1
Nitric	HNO_3	1	1	1	1	1	1
Nitrous	HNO_2	Indicator destroyed	1	—	1	0	?
Sulphuric	H_2SO_4	2	2	2	2	2	2
Sulphurous	H_2SO_3	1	2	—	—	—	2
Thiosulphuric	$H_2S_2O_3$	2	2	2	2	2	—
Sulphydric	H_2S	0	1 (dilute)	0	—	0	?
Boric	H_3BO_3	0	—	—	—	—	1
Carbonic	H_2CO_3	0	1 (dilute)	0	—	0	2
Silicic	H_4SiO_4	0	—	—	—	—	?
Phosphoric	H_3PO_4	1	2	—	—	—	3 (nearly)
Arsenic	H_3AsO_4	1	2	—	—	—	3 (nearly)
Arsenious	H_3AsO_3	0	—	—	0	0	3
Chromic	H_2CrO_4	1	2	2	—	0	?
Acetic	$HC_2H_3O_2$	—	1	—	1 (nearly)	—	1
Butyric	$HC_4H_7O_2$	—	1	—	1 (nearly)	—	1
Valeric	$HC_5H_9O_2$	—	1	—	1 (nearly)	—	1
Lactic	$HC_3H_5O_3$	—	1	—	1	—	1
Oxalic	$H_2C_2O_4$	—	2	2	2	2	2
Succinic	$H_2C_4H_4O_4$	—	2	—	2 (nearly)	—	—
Tartaric	$H_2C_4H_4O_6$	—	2	—	2	—	2
Citric	$H_3C_6H_5O_7$	—	3	—	—	—	3
Carbolic (phenol)	HC_6H_5O	0	—	—	0	—	1
Picric	$HC_6H_2N_3O_7$	—	1	1	—	—	1
Benzoic	$HC_7H_5O_2$	—	1	1	1	—	1
Salicylic	$HC_7H_5O_3$	—	1	1	1 nearly)	—	1
Hydrocyanic	HCN	0	0	—	0	—	1
Hydroferrocyanic	$H_4C_6N_6Fe$	4	4	—	4	—	—
Hydroferricyanic	$H_3C_6N_6Fe$	3	3	—	3	—	—
Thiocyanic	$HSCN$	1	1	—	1	—	1
Uric	$H_2C_5H_2N_4O_3$	0	1	1	—	—	?

[1] HBr, HI, and HF (probably) behave like HCl.

were uncombined, and hence the amount of acid in salts of aconitine. cinchonine, brucine, strychnine, morphine, quinine, quinidine, urea, etc., operating if necessary in alcoholic solution, can be ascertained by titration with standard alkali just as if no organic base were present.

Until a few years ago, the behaviour of the alkaloids with indicators had been very incompletely studied, and their titration with standard acid was rarely attempted. Where this is desired, phenolphthalein is inapplicable for their direct estimation, in nearly all cases; good results are, however, obtained with sparteine and fair results with coniine (Kippenberger, *Zeit. anal. Chem.*, 1900, **39**, 201).

Kippenberger (*loc. cit.*) studied the degree of accuracy obtainable in the case of different alkaloids by direct titration in the presence of various indicators. The following table taken from the results, gives the most suitable indicator for use in each case.

Atropine: Lacmoid, uranin.
Morphine: Cochineal, lacmoid.
Aconitine: Azolitmin (litmus).
Veratrine: Lacmoid.
Thebaine: Iodeosin, cochineal.
Codeine: Iodeosin, lacmoid.
Emetine: Iodeosin, cochineal.
Cocaine: Lacmoid.
Strychnine: Azolitmin.
Brucine: Cochineal.
Nicotine: Lacmoid, iodeosin.
Coniine: Iodeosin, cochineal, lacmoid.
Sparteine: Hæmatoxylin.
Quinine: Azolitmin, hæmatoxylin.
Pelletierine (*punicine*): Cochineal.
Papaverine: Lacmoid.
Narcotine: Lacmoid.
Narceine and *caffeine:* None suitable.

For the use of a series of substituted and sulphon-phthaleins as indicators covering different ranges of acidity ("hydrogen ion" concentration) and a complete bibliography of the question see Clarke's "Determination of Hydrogen Ions."

The remarkably delicate indicator iodeosin (erythrosin), which was introduced by Mylius and Förster (*Ber.*, 1891, **24**, 1482) as a means of estimating the minute traces of alkali dissolved from glass by the action of water, is particularly useful as an indicator in the titration of some alkaloids, as for instance in Toth's method of estimating nicotine in tobacco. The methods used in dealing with alkaloids are described in detail in another volume.

Tetraiodo-phenolphthalein, $C_{20}H_{10}I_4O_4$, is obtained by the direct action of iodine on a solution of phenolphthalein. It forms a pale yellow, odourless, tasteless powder, melting at 255° with decomposition and evolution of iodine. It is insoluble in water or alcohol, but is dissolved by ether and chloroform. It combines with alkalies to form soluble salts.

Tetraiodo-phenolphthalein contains 60% of iodine, which is not liberated by the action of alkalies or dilute acids, even on boiling. It is employed in medicine under the name of "*Nosophene*," and has been found valuable in skin-diseases. "*Antinosin*," the sodium salt of nosophene, is a bluish powder which is readily soluble in water, and has been found useful as an antiseptic dusting powder and internally in catarrh of the stomach and intestines.

"Endoxin," the bismuth salt of tetraiodo-phenolphthalein, is a brownish-red, odourless and tasteless powder soluble in alkalies with bluish-violet colour. It is employed as an internal antiseptic.

Gallein, $C_{20}H_{12}O_7$, obtained by heating pyrogallol and phthalic anhydride to 190° to 200°, forms a brownish-red powder, or green crystals of metallic lustre which are almost insoluble in water, but soluble in alcohol. Gallein is a weak acid, forming with alkalies a blue solution which becomes dirty-coloured on standing. Gallein dissolves in ammonia with violet colour and the solution gives violet precipitates with metallic salts.

When heated at 200° with 20 times its weight of strong sulphuric acid, gallein loses the elements of water and is converted into:

Cœrulein, $C_{20}H_{10}O_6$, which on pouring the cooled solution into water is obtained as an amorphous black precipitate. It is nearly insoluble in water (which it colours olive-brown), alcohol, or ether, but dissolves easily in acetic acid. In commerce, cœrulein occurs as a thick dark coloured paste. In alkalies it dissolves with beautiful grass-green colour, and the solution gives with mordants very stable lakes. With strong sulphuric acid cœrulein gives a dirty brown colour. On warming cœrulein with ammonia and zinc powder, a brownish-red solution is formed, containing *cœrulin*, $C_{20}H_{12}O_6$. The solution is oxidised on exposure to air, the original green colour being restored. Cœrulein may be employed in dyeing in the same manner as indigo.

On treating cœrulein paste with 2 molecules of sodium hydrogen sulphite ($NaHSO_3$), a colourless compound of the two is formed, which can be removed from the unaltered cœrulein by extraction with cold alcohol. The bisulphite compound of cœrulein occurs in commerce as a black powder under the name of *Cœrulein S* It dissolves in water with greenish-yellow colour, and on boiling the solution becomes deep green, and sulphurous acid is evolved. Acids and alkalies effect the same decomposition in the cold.

Cœrulein and its bisulphite compound are used for dyeing and printing cotton fabrics, on which they produce various shades of green. The colour is not removed from the fibre by boiling with soap or alkali hydroxides and is darkened by concentrated hydrochloric acid. The most characteristic test for cœrulein is that with a warm acid solution of stannous chloride, which turns the fibre brownish-red owing to the formation of cœrulin. On then washing with water, or preferably with a very dilute solution of bleaching-powder, the original green colour is restored.

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MODERN EXPLOSIVES

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INTRODUCTORY

An explosive is a material which is capable of giving off a very large volume of gas very suddenly; at the same time it always evolves a great deal of heat. The gas which is thus suddenly formed tends naturally to expand, and in so doing to overcome the resistance of anything which opposes the expansion. The sharp noise, which is always associated with an explosion, is due to this sudden evolution of gas. Heat is liberated at the same time, and this produces a bright light; it also increases the expansion of the gas.

A great many explosives are now known. Some are single substances from the chemical point of view, such as nitroglycerin or fulminate of mercury; others are mixtures, of which the most familiar example is ordinary gunpowder (black powder). In mixed explosives some or all of the ingredients may be themselves explosive. Some explosives are very violent, detonating at the rate of several miles per second; these are termed high explosives. Others burn comparatively slowly and are used to propel a bullet or shell from a fire-arm; these are the smokeless powders. Black powder occupies a position between these two classes.

Some can be exploded directly by the application of a spark or friction; gunpowder, if in a fine state of division, can be ignited by a spark, fulminate of mercury either by a spark or a blow or friction. Other explosives require a small quantity of an explosive of the last kind to send them off satisfactorily; high explosives are usually detonated by means of a detonator charged with fulminate; smokeless powders also are generally provided with a small igniting charge of a more sensitive explosive. Fireworks are charged generally with slow burning mixtures resembling gunpowder more or less.

Explosives may be classified in various ways, according to the purpose of the classification, but the great majority of them fall naturally into two main divisions: propellants and high explosives. Propellants explode comparatively slowly, and are used to propel projectiles from fire-arms. High explosives are much more rapid in their action, and are used for bursting and shattering. Propellants are of two sorts, according as they are intended for use in shot-guns or rifled fire-arms. Those for shot-guns burn more rapidly than those for the latter, but both practically always contain a considerable proportion of nitrocellulose, gelatinised by means of such solvents as acetone or ether-alcohol, according as it is of high or low nitration. Some contain also nitroglycerin, and are then called nitroglycerin powders, whereas those that do not contain this substance are termed nitrocellulose powders. Many powders also contain other ingredients.

Of high explosives an important class is used for charging shells and bombs. As a rule, but not necessarily, these are not the same as the explosives used for mining operations and other general blasting purposes. Another important class is that of the coal-mine explosives, which are designed to give only a short and comparatively cool flame so as to diminish the danger of igniting fire-damp and coal-dust.

Of the various physical properties of an explosive, one of the most important is its sensitiveness. It must be sufficiently sensitive to be fired with certainty by the means to be used, but up to this limit the less sensitive it is, the safer and therefore the better it is. An explosive that is very sensitive to blow or friction is too dangerous for use. The hardness, consistency and form of grain are all of importance as they affect the explosive properties.

Other important properties are the power and violence of the explosive. The power is the quantity of work that the explosive can do. The violence depends not only on the power, but also on the time in which the energy is set free.

CELLULOSE NITRATES

The form of cellulose used for the manufacture of explosives and celluloid is generally cotton, although wood cellulose is also used. All commercial nitrocellulose is made by nitrating with a mixture of nitric and sulphuric acids, in which the latter usually predominates.

The stability and nature ot the nitrocotton are considerably affected by the method used in its manufacture, as also by the quality of cellulose employed, and other details of preparation. After nitration the material is thoroughly washed, boiled for some days with frequent changes of water and pulped in a machine resembling a papermaker's poacher or beating engine.

Properties of Nitrocellulose.—The true sp. gr. is given by Mosenthal as 1.65 to 1.68 (*J. Soc. Chem. Ind.*, 1906, **26**, 443). Ordinary compressed blocks containing much water and air have a sp. gr. of 1.0 to 1.2, but if highly compressed for blasting purposes it may be as high as 1.4. The compressed material resembles wood pulp. When it has been gelatinised with a solvent it resembles horn, but is tougher and harder. It is slowly saponified by alkalies and is reduced to cellulose by potassium and ammonium hydrosulphides, sodium stannate, sulphides, polysulphides, and thiocarbonates. It is somewhat hygroscopic. Will showed that if n is the percentage of nitrogen in a sample of nitrocotton, and h the percentage of moisture it takes up in saturated air at 25°, $n + h = 14.6 \pm 0.1$. Even good nitrocellulose decomposes at all temperatures, giving off carbon monoxide and nitrogen oxides. The rate of decomposition increases rapidly with rise of temperature, and is about doubled for every increase of 5°. (Will.)

In England cotton waste is used for the manufacture of the guncotton required for the cordite of the army, but for the Navy sliver is employed. The collodion cotton for blasting gelatine is mostly made from cop bottoms. All these have to pass strict specifications. In America linters are generally used and the same form of cotton is also in use on the Continent. Wood cellulose has been used for many years for some brands of sporting powders and during the war the Germans employed it on a very large scale for their military powders, and they have claimed that it is, on the whole, as suitable as cotton or even better. Sulphite cellulose is the best and it is made into the form of thin crape paper which is torn into small pieces.

When guncotton is to be used for the manufacture of other explosives it is usually moulded in hydraulic presses into blocks of various shapes containing 30 to 40% of water. When used by itself as a blasting explosive it is compressed strongly until it is as hard as hard wood and contains about 20% of moisture. That used by the

British Government is a nitrocotton containing about 13% of nitrogen mixed with a little phenol and calcium carbonate to prevent decomposition. Small cylinders of the same material, but dried, are also used as primers for firing charges of wet guncotton. Nitrated cotton yarn impregnated with rubber solution is also used as a priming charge for certain sorts of ammunition.

Nitrogen.—According to the strength and composition of the acids and other conditions of nitration, nitrocelluloses can be obtained with very different proportions of nitrogen and differing in many of their properties. It is possible in the laboratory to prepare a guncotton containing 14% of nitrogen, which almost agrees with the formula for the trinitrate $C_6H_7(N_3O)_3O_2$, but this compound is very unstable and breaks down even on standing at the ordinary temperature for a few weeks, leaving a lower nitrate. (See Lunge and Bebie, *J. Soc. Chem. Ind.*, 1901, **14**, 514.) On the manufacturing scale it is hardly practicable to produce a nitrocellulose containing more than 13.5% of nitrogen, and commercial guncotton seldom contains more than about 13%. The guncotton used for making cordite is specified to contain 12.8 to 13.1%. Nitrocottons used for making other smokeless powders for sporting and military purposes generally contain percentages of nitrogen from 12.4 up to 12.8%. Collodion cotton for blasting gelatin contains 12.0 to 12.3%, for celluloid, varnish, and for artificial silk still lower nitrates are used. Various writers have endeavoured to classify nitrocelluloses according to their chemical formulæ; assuming the cellulose molecule to be of some particular size, $C_6H_{10}O_5$ or $C_{12}H_{20}O_{10}$ or $C_{24}H_{40}O_{20}$, they have divided the nitrocelluloses into tri- and di-nitrates, or penta-, tetra-, and tri-nitrates, etc., but as no fixed limits can be drawn between the different classes, and products can be obtained with any desired percentages of nitrogen, it is better to specify the nitrocelluloses according to their percentages of nitrogen, solubility in ether-alcohol, and other properties.

Detection of Nitrocellulose.—This depends whether the substance has been gelatinised with a solvent or not. Practically all propellants contain nitrocellulose wholly or partly gelatinised. Many of them consist practically entirely of nitrocotton, and most of them contain at least 50%. Gelatinised nitrocellulose can be recognised by its hard, tough nature; unless mixed with liquid material, such as nitroglycerin it is tougher than horn. It may be distinguished from other substances by the fact that it is insoluble in water, alcohol, or ether, but soluble in acetone and ethyl acetate. The various nitrocottons can be distinguished from one another, after isolation, by the percentage of nitrogen and of matter soluble in a mixture of alcohol and ether.

Ungelatinised nitrocellulose can be recognised by the structure of the fibres, which is almost the same as that of the unnitrated material. There is, however, a distinct difference in colour when the fibres are examined in polarised light. (See H. Ambronn, *Kolloid Z.*, 1913, **13**, 200.)

Estimation of Nitrocellulose.—This is usually done by extracting the explosive with one or more of the solvents in which nitrocellulose is insoluble and then weighing the residue of nitrocellulose. The first extraction is nearly always with ether, and in many cases no further extraction is needed. If mineral nitrates are present, a further extraction with water is necessary, and in many cases an extraction with benzene is required to remove organic substances. About 2 grm. of the explosive are weighed out into a filter-paper or thimble and extracted in a Soxhlet with ether (sp. gr. 0.72). The filter-paper and contents are then dried in a water-oven to constant weight, and the weight of the filter-paper or thimble is deducted. The material used for this analysis should be so finely ground that it passes through the finer sieve of the nest used for the heat test. This material should be allowed to soak in the ether all night, and then extracted with it for about 2 hours.

In some cases, if the percentage of nitrogen in the nitrocellulose is known, it may be estimated indirectly by a nitrogen estimation.

EXAMINATION OF NITROCELLULOSE

The estimation of nitrogen in guncotton is generally carried out by means of a Lunge nitrometer provided with a cup and graduated from about 100 to 150 c.c. It is filled with mercury, the bottom of the tube being connected with a compensating tube by means of rubber tubing with canvas insertion. The guncotton is dried in a water-bath to constant weight, 0.5 grm. or more is weighed out, according to the percentage of nitrogen, precautions being taken that moisture is not absorbed during the weighing, as the material is very hygroscopic. It is then transferred to the cup of the nitrometer, and

5 c.c. of chemically pure sulphuric acid of 92.5 to 94% strength are added. The material is stirred with a small glass rod, run into the nitrometer, and is rinsed in several times with sulphuric acid, using for this purpose 10 c.c. in three portions, taking care to introduce no air. After being allowed to stand for a quarter to half an hour the bulb is shaken vigorously so as to bring the mercury and acid into intimate contact. After a short time nitric oxide is evolved. The shaking is continued until the evolution is practically complete. Then the nitrometer is allowed to stand until the acid and mercury have separated from one another, and the shaking is repeated. After standing for about ½ hour to cool, the volume is adjusted to atmospheric pressure and read, as also the temperature and barometric pressure, the volume is corrected to N.T.P., and the percentage of nitrogen in the guncotton is calculated. In this, as in all operations with the Lunge nitrometer, the result depends to some extent on the exact method of shaking, and it is only after some practice that the operator can obtain results approaching the theoretical. Beginners almost invariably obtain results which are too low.

There are various small sources of error in the nitrometer method: carbon monoxide and dioxide are evolved, and some of the nitric oxide is reduced to nitrous oxide, nitrogen and ammonia and some is dissolved by the acid. These have been investigated by E. G. Beckett *J. Soc. Chem. Ind.*, 1914, **33**, 628; *Trans., Chem. Soc.*, 1920, **117**, 220, in continuation of the work of M. Marqueyrol and D. Florentin (*Bull. Soc. Chem.*, 1911, (iv), **9**, 234 and he recommends the procedure here described. Previously the strength of sulphuric acid generally used was 96%. A. Hervé recommends that the final strength of the acid in the nitrometer be adjusted to 85% in order to reduce the solubility of the gas. (*Monit. Scient.*, 1918, **62**, 241). In America the larger and more complicated Du Pont nitrometer is used (W. Cope and G. Taylor, *Technical Paper* 160 *of U. S. Bureau of Mines*), but this has not found favour in Europe.

Low results are obtained in the presence of camphor, diphenylamine, mononitrotoluene and other substances which are liable to be nitrated under the conditions that exist in the nitrometer.

The *Schultze-Tiemann* method is also used extensively in many laboratories for the estimation of nitrogen. It usually gives results

0.1 or 0.2% higher than the Lunge nitrometer. It is specially useful for the analysis of guncottons that have not yet undergone purification by boiling, as the nitrometer gives very low results for these. They evidently contain some unstable impurities, which interfere with the reaction of the mercury. The following are the details of the method as carried out at the Dartford factory of Messrs. Curtis's and Harvey:

0.5 grm. of the dry nitrocellulose and 30 c.c. of boiling water are introduced into a flask of about 200 c.c. capacity fitted with rubber cork, through which pass two tubes. One of these leads into the lower end of a graduated tube of 150 c.c. capacity, and the other is used to introduce liquid into the flask. Both tubes have rubber connections which can be closed by means of pinchcocks. Air is expelled from the flask and tubes by boiling the water in it energetically for some time, and the pinchcocks are closed. Then the graduated tube is placed in position, 20 c.c. of hydrochloric acid and 20 c.c. of strong ferrous chloride solution are boiled in a test-tube and then the contents are drawn into the flask, care being taken not to admit any air. A little boiling water is added to wash out the test-tube, the admission tube is closed by means of its pinchcock, the contents of the flask are boiled gently, and the other tube, leading to the measuring tube, is opened. The gas comes off and passes into the measuring tube, which has been filled with strong sodium hydroxide solution and stands in a bath of the same liquid. The evolution lasts about 15 minutes. Some more boiling water is then run into the flask to wash down any particles of unattacked nitrocellulose and the contents are then boiled again, this procedure being continued until there is no further evolution of gas. The orifice of the graduated tube is next covered with the thumb or finger protected with a rubber finger stall, and removed to a large cylinder containing water, where it is allowed to cool. The tube is adjusted so that the water is at the same level inside and out, the volume of nitric oxide is then read, corrected for temperature and pressure, and calculated to percentage of nitrogen. See also Jacquè (Report of Sixth Int. Cong. Ap. Chem., Vol. I, 265).

The *Dumas* method can also be used if precautions are taken to prevent the nitrocellulose from burning too rapidly; it must be mixed with a large quantity of inert material. The method is, however, seldom used for this purpose.

Solubility.—All nitrocelluloses are soluble in acetone, ethyl acetate, amyl acetate, and some other organic solvents. They are all insoluble in water and benzene, and all but the very low nitrated products are insoluble in either pure ether or alcohol, although commercial nitrocelluloses give up a small amount of fatty matter to ether, and resinous matter and decomposition products to alcohol. It should, however, be noted that commercial ethers usually contain a small proportion of alcohol, and if an ether of this kind be used, some of the nitrocellulose will be dissolved. The sp. gr. of ether used for extracting fatty matter and nitroglycerin from nitrocellulose should not exceed 0.720.

The different nitrocelluloses are characterised by different degrees of solubility in a mixture of ether and alcohol. The highest nitrated products are practically insoluble in the mixed solvents. Guncottons containing 13% of nitrogen give up about 8 or 10%, and as the percentage of nitrogen further falls the solubility rapidly increases, until with nitrocottons containing about 12.3% of nitrogen solubility is practically complete. The degree of solubility is, however, not conditioned solely by the percentage of nitrogen, but also depends upon the proportions of nitric and sulphuric acid used in nitration, and other details of preparation.

The degree of solubility in ether-alcohol is a matter of importance in the manufacture of smokeless powder, especially if it is to be gelatinised with this solvent. Collodions that are to be used for varnishes or for photographic plates must be completely soluble and must give clear sols free from lumps and specks. The solubility depends not only on the relative proportions of ether and alcohol, but also on the amount of water present and on various impurities. In mixtures very rich in ether a little water increases the solubility, but in those rich in alcohol it has the opposite effect. The presence of methyl alcohol or methyl ether increases the solubility, whereas the substitution of higher members of either series renders nitro-celluloses less soluble. A considerable amount of work has been done of late years on this subject but there still remains much to be cleared up. .

For testing guncotton to be used in the manufacture of cordite the following method is used: of the dry guncotton 4 grms. are weighed out and placed in a stoppered graduated cylinder of 200 c.c. capacity, and to it are added 150 c.c. of a mixture of 2 volumes of pure ether of sp. gr. 0.720 and 1 volume of pure alcohol of sp. gr. 0.830 at 15.5°/15.5°. The cylinder is shaken at frequent intervals, or continuously on a shaking machine, for 6 hours whilst the temperature is maintained at 15.5°. It is then allowed to settle and 75 c.c. are drawn off, the solvent is evaporated, and the residue is dried to constant weight at 65°.

The German official method is somewhat similar: 2 grm. of the fine, sifted and well dried nitrocellulose are placed in a stoppered 500 c.c. cylinder and to it are added 215 c.c. of alcohol (sp. gr. 0.816 at 15°) and then 285 c.c. of ether (sp gr. 0.720). This is shaken frequently for 5 hours and then allowed to settle. 250 c.c. of the clear liquid are drawn off, about 10 c.c. of water are added, the solvent is evaporated cautiously, and the residue is dried for half an hour at 80° and weighed.

Both these methods must give somewhat high results, as the whole of the solvent cannot be driven off in the manner prescribed; but this is not a matter of great importance, as the results are only intended to be comparative. With nitrocelluloses, which are almost entirely soluble, it is better to weigh the residue instead of the dissolved matter. The following is the method prescribed for the soluble nitrocotton used for making the United States smokeless powder.

0.5 to 1 grm. of the finely divided dry sample is treated, with frequent stirring, in a stoppered vessel with 350 c.c. of a a mixture of pure ethyl alcohol and pure ethyl ether, the sp. gr. of the mixture being from 0.748 to 0.750 at 20°. The residue is allowed to settle and the supernatant liquid syphoned off. The extraction with ether-alcohol solution is repeated twice; the insoluble residue is poured into a tared Gooch crucible having a thin asbestos filter, and well washed with ether-alcohol. The residue is then partially dried at 80°, and the drying completed by exposure to a temperature of 100° till the weight is constant. The per cent. of insoluble matter subtracted from 100 gives the per cent. of soluble nitrocellulose.

The following rapid method has been found by E. C. Worden (Technology of Cellulose Esters, 1921, I, 2207) to be satisfactory for pyroxylenes that are to be used in solution: 5 grm. of the air-dry sample are dissolved in 100 c.c. of the particular solvent mixture that it is to be used, or if the viscosity be high the volume of solvent may be increased to 200 c.c. The glass-stoppered flask is shaken frequently, either alone or after the introduction of a known weight of shot or glass beads, until all that will dissolve has gone into solution. Allow it to stand 4 hours, or until the sediment has deposited, and decant the clear liquid carefully. Add 100 c.c. of the solvent to the residue in the flask, shake vigorously, filter through a Gooch crucible or tared filter, dry at 100°, weigh and deduct the weight of beads or shot. Usually 1 to 1½ hours drying suffices. Where quick and approximate determinations are to be made a portion of the 5% solution is placed in a 10 c.c. urinary tube graduated in 1/10 c.c. and centrifuged for 15 minutes at the highest speed. The volume of the residue may now be read off and converted into per cent. from the results of a series of comparative tests.

In France, in order to ascertain the suitability of a batch of nitrocellulose (CP_2) for the manufacture of a particular variety of Poudre B and its uniformity with other batches, the solubility is determined in a mixture of amyl alcohol and ether to which an amount of water is added according to the sort of nitrocellulose. 0.5 grm. of the nitrocotton and 25 c.c. of the ether-amyl alcohol are placed in a corked vessel in a thermostat at 20° for 2 days with occasional shaking. 5 c.c. of the clear liquid are then withdrawn and evaporated. The per cent. of soluble matter is called "*coefficient de gelatin-isation*" and is found to vary inversely with the amount of ether-ethyl alcohol required to gelatinise the material. (Abderhalden, Mèm. Poudres, 1921, **18**, 183.) This method has been adopted because the nitrocelluloses are almost entirely soluble in ether-ethyl alcohol and consequently solubility in this solvent would reveal practically no differences. In England the same object has been attained by determining the viscosity of solutions.

Matter Insoluble in Acetone.—The matter insoluble in acetone consists mostly of unnitrated or very imperfectly nitrated fibres. To estimate it, 2 grm. are treated with about 150 c.c. of acetone for 6 or 8 hours with occasional shaking. It is then allowed to stand over-night and the clear liquid is carefully decanted. The residue is washed several times by decantation with acetone, then transferred to a tared filter, washed again, dried in the water-bath, and weighed.

Unnitrated fibre is sometimes estimated by repeated treatment with sodium sulphide solution, which attacks the nitrocelluloses, but leaves the unnitrated cellulose unaffected. Lunge and Weintraub, however, found the method unsatisfactory, and recommend instead the use of sodium ethylate, which acts in a somewhat similar manner (*Zeits. ang. Chem.* (1899), **12**, 473). The method is specially useful in the case of products which contain a considerable proportion of matter insoluble in acetone.

In 100 c.c. of ordinary alcohol dissolve 3 grm. of sodium, and if the liquid is not quite clear, filter. Add 100 c.c. of acetone, and of the mixture set aside 50 c.c. Into the remaining 150 c.c. introduce about 5 grm. of the nitrocellulose. The action is hastened by warming on a water-bath to 40 or 50° with occasional agitation. In 20 or 30 minutes the action is complete; the brownish-red liquid is allowed to settle, and decanted through a small filter-paper, and the residue is washed by decantation with alcohol to remove any condensation products of acetone, then with hot water, and finally with water containing a little hydrochloric acid. If the amount of unnitrated cellulose is considerable or if a high degree of accuracy is not desired, this first treatment may suffice. The cellulose contained evolves no gas in the nitrometer, but gives a strong reaction with diphenylamine, showing that traces of nitrocellulose are still present. It may, therefore, be desirable to repeat the extraction. For this purpose the residue is first washed with alcohol to displace the water, and is then washed off the filter with 50 c.c. of the acetone ethylate solution set aside as above. The remainder of the above treatment is then repeated and finally the cellulose is washed with water, dried at 100°, and weighed. It now only gives a slight blue coloration with diphenylamine. The cellulose residue should only have a very slight brown colour, which may be removed by treatment with bleaching solution. A good nitrocellulose contains hardly any unnitrated fibre.

In the United States "unaltered cellulose" is estimated by boiling a little with sodium stannite solution, washing thoroughly with warm water and drying. The reagent should be prepared freshly by adding sodium hydroxide solution to stannous chloride until the precipitate first formed is just redissolved. (Worden, Technology or Cellulose Esters, Vol. I; pt. 3 (1921), 2295.)

Free Acid and Alkali.—These may be estimated by extracting the finely divided material with hot water, filtering, and titrating in the usual way. Very thorough washing is necessary, as the material has the property of adsorbing considerable quantities of acid and alkali. When testing for minute traces it is necessary carefully to examine the water and other materials used.

Nitrocellulose usually contains more or less calcium carbonate, which has either been added intentionally or has been precipitated from the water used for boiling the material during the purification. To estimate this digest a known weight of the sample with a known volume of standard hydrochloric acid, filter, wash thoroughly and titrate. using methyl-orange or other suitable indicator.

If the quantity of calcium carbonate be very small it is practically impossible to obtain consistent results by this method as part of the acid is retained obstinately by the nitrocellulose. It is better therefore to neutralise it almost with standard alkali before filtering and finish the titration after filtering and washing.

Old or imperfectly stabilised material sometimes becomes acid. The acidity may be estimated in a similar manner.

Discoloration.—Really pure nitrocellulose, when ungelatinised, is quite white, but it has often a slight brown tint due to oxide of iron precipitated in the fibres during manufacture. When stored in a wet condition it frequently becomes quite black, especially on the surface, in consequence of bacterial action. The bacteria, however, attack mostly the paper or other organic material in contact with the nitrocellulose. This discoloured nitrocellulose generally gives a low heat test.

In Germany mercuric chloride is sometimes added to the nitrocellulose to kill the bacteria, but in England this is not allowed as it masks the heat test. Carbolic acid is added instead to compressed wet guncotton intended for demolitions.

Ash.—The guncotton is mixed in a large crucible with paraffin wax and paraffin oil which is set alight, a small flame being kept going underneath. As the mixture burns away, more wax is added from time to time. The flame must not be allowed to come in contact with the guncotton itself until it has been broken down by the heat. Finally the crucible is ignited to destroy all organic matter, cooled and weighed.

Guncotton and nitrocellulose used for the manufacture of cordite must not contain more than 1% of mineral matter. This, however, consists largely of calcium carbonate. Many nitrocelluloses do not contain more than 0.2 to 0.4% of ash.

Another method is to decompose the explosive with nitric acid. Shrimpff places about 5 grm. in a large crucible with 25 c.c. of pure nitric acid (sp. gr. 1.4) evaporates down and ignites cautiously. After cooling, a little water is added, and the contents are again evaporated and ignited. (*Nitrocellulose*, 1919, 108.)

Microscopic Examination.—It is best for this to embed the material in Canada balsam or moisten it with 50% alcohol. In polarised light the fibres appear of various colours depending upon the degree of nitration and conditions of manufacture, and can readily be distinguished from unnitrated cellulose and foreign matter. For details of this and other optical properties see Mosenthal (*J. Soc. Chem. Ind.*, 1907, **26**, 1, also H. Ambronn *Kolloid Z.*, 1913, **13**, 200).

Sulphuric Esters.—It was shown by Cross, Bevan, and Jenks (*J. Soc. Chem. Ind.*, (1905), **24**, 379; *Ber.*, 1901, **34**, 2496) that during the process of nitrating cotton a small proportion of mixed sulphuric-nitric esters of cellulose are formed, and it was demonstrated by Hake and Lewis (*J. Soc. Chem. Ind.*, 1905, **24**, 374 and 914) that these substances are considerably less stable than the pure nitric esters. They are decomposed only very slowly by boiling with alkaline water, but are readily hydrolised by acid. Hence the necessity of having the first waters acid in the boiling of guncotton (See R. Robertson, *J. Soc. Chem. Ind.*, 1906, **25**, 624).

To ascertain the amount of combined sulphuric acid in nitrocotton take 5 grm. of it and heat it gently on a water bath with 50 c.c. of concentrated nitric acid until it is dissolved. After cooling add about a gram of sodium or potassium chlorate and evaporate to dryness. Treat the residue with 20 c.c. of concentrated hydrochloric acid and about 0.5 grm. chlorate and again evaporate to dryness. The treatment with hydrochloric acid and chlorate is repeated, and the sulphate in the residue is then estimated by precipitation with barium chloride. The amount expressed as H_2SO_4 should not exceed 0.1%.

This of course gives the total sulphur in the nitrocellulose, and some, of it may be present as inorganic sulphates. To overcome this difficulty Schrimpff divides the solution from the above process into two portions and estimates the sulphate in one and the calcium in the other. The calcium carbonate is estimated separately as already described, the remainder of the calcium is calculated as calcium sulphate and the sulphate left over from this is reckoned as sulphuric ester and calculated at H_2SO_4.

Viscosity of Solutions of Nitrocellulose.—This is an important quality, as it influences more or less the use of the material for all purposes. Although a considerable number of papers have been published dealing with it, their value is diminished by the fact that most of the results are not comparable with those of other workers, being expressed in seconds flow in an arbitrary instrument or a ratio to the time of flow of the solvent itself. The latter method does allow of some comparisons but is not very satisfactory as in an orifice viscometer such as that of Ostwald, the true viscosity is not quite proportional to the times when these differ very greatly. Viscosimeters in which the liquid is made to flow through an orifice are liable to give erratic results with solutions of nitrocellulose because they may contain small lumps or specks which impede the flow. W. H. Gibson and L. M. Jacobs have, however, described a falling sphere viscosimeter) (*Trans. Chem. Soc.*, 1920, **117**, 473), the readings of which can be converted readily into true viscosity, η.

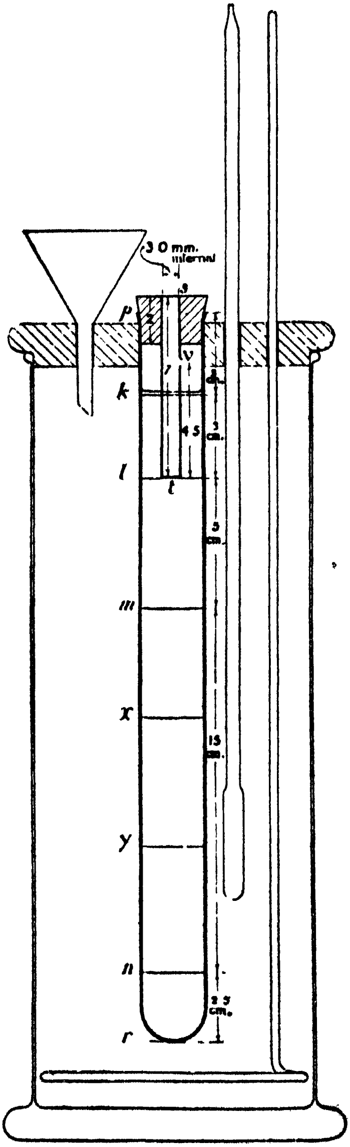

FIG. 24.—Falling sphere viscosimeter. (Trans. Chem. Soc.)

The apparatus consists of a glass tube 29 cm. long and 2 cm. internal diameter, sealed at the bottom. It has horizontal marks at 6, 11, 16, 21 and 26 cm. from the top, and is closed by a rubber cork through which passes the releasing tube 3 mm. internal diameter and 6 cm. long. This is adjusted to dip 3 cm. below the surface of the liquid and has a small hole in the side to equalise the air pressure inside and out. The long glass tube is mounted truly vertically inside a water bath which is maintained at 20°. The falling spheres consist of ball bearings 1/16 in. diameter (0.1588 cm.). One of these is released and the time is taken with a stop watch between the marks *m* and *n*, 11 and 26 cm. from the top. The viscosity is then given by the equation

$$9\eta l(1 + 2.4x)(1 + 3.3\frac{r}{h}) = 2gr^2(s - \sigma)T$$

where η is the viscosity in C. G. S. units, x is the ratio of the radius of the sphere to that of the tube, r is the radius of the sphere, s its density, σ the density of the liquid and h its height (25.5 cm. in this case), g is gravity (981) and T is the time the sphere takes to fall through the distance l (15 cm.).

The instrument can also be standardised against a liquid of known viscosity, such as castor oil, for which $\eta = 9.89$ at 20°. In that case use can be made of the simplified equation $\eta = K(S - \sigma)T$, where K is a numerical constant involving all the corrections for the particular tube.

For a discussion of the results of investigations in this connection see Applied Chemistry Reports, 1920, V, 539 and 1921, VI, 569, where references will also be found.

Stability Tests.—For these see below at end of chapter.

NITROSTARCH

This material, which should more correctly be termed starch nitrate, has been proposed repeatedly as an explosive but most attempts to introduce it have been given up again on account of the difficulties in manufacture and stabilisation. In the United States, however, the Trojan Powder Co. makes a whole series of blasting explosives containing this substance, and it is claimed that the difficulties have been overcome.

Under the name of Grenite it was used for filling hand grenades (E. C. Worden, *Technology of Cellulose Esters*, 1921, Vol. I, 1837), small proportions of heavy hydrocarbons and gum arabic being added to it. Trojan Grenade Powder, which was used on a larger scale, consisted of a mixture of starch nitrate, ammonium nitrate, sodium nitrate and small quantities of charcoal, heavy hydrocarbon, "antacid" and diphenylamine (Worden, *loc. cit.;* C. E. Munroe and S. P. Howell, U. S. Bureau of Mines, Reports of Investigations, June, 1920; *J. Soc. Chem. Ind.*, 1920, **39**, 641A).

It is not authorised in Great Britain and cannot therefore be used there.

Starch from Indian corn is the variety which is found to be most suitable. The form of the granules, as seen under the microscope, is little affected by nitration, but the nitrated product can be distinguished by the fact that it does not give a blue coloration with iodine.

Nitrostarch is a slightly yellowish powder, the sp. gr. of which is stated to be about 1.1 (U. S. Bureau of Mines Bul., 1923, **219**, 88); it contains 12 to 13.3% N with a mean of about 12.6%. Its solubility and other properties resemble those of the nitrocelluloses, and it is estimated and examined in much the same way. In America the nitrogen is estimated with the Du Pont modification of the Lunge nitrometer, but H. Kesseler states that this gives low results in consequence of the poor solubility in sulphuric acid. (*Z. angew. Chem.*, 1922, **35**, 145). The Schultze-Tiemann method is also unsatisfactory because the granules adhere to the walls of the vessel. He therefore uses the following method: about 0.25 grm. of the material is moistened with alcohol, and 5 c.c. of 50% potassium hydroxide solution are added at 40 to 50°. When, in a few hours, solution is complete the liquid is transferred to a 500 c.c. distillation flask together with some water, 50 c.c. of 33% sodium hydroxide and 1.5 grm. Devarda alloy (Cu 50, Al 45, Zn 5). The reaction is started by warming gently, and when it is complete the ammonia formed is distilled into a receiver containing N/10 sulphuric acid, which is then titrated back with N/10 sodium hydroxide, Methyl Red being used as indicator This method works satisfactorily also with nitroglycerin, nitrocellulose, nitroglycol and ethyl nitrate.

NITROGLYCERIN

$C_3H_5(NO_3)_3$ mol. wt. 227.1

When glycerol is gradually added to a well-cooled mixture of strong nitric and sulphuric acids, it is converted into propenyl nitrate, or nitroglycerin. When great care is taken, nearly the theoretical yield is obtainable; but if the temperature is allowed to rise, more complex reactions ensue, with formation of oxalic acid, glyceric acid, etc., and if the action is very violent, spontaneous explosion may take place. This may also occur if the glycerol is impure.

Nitroglycerin is a heavy oily liquid which, when pure, is colourless, but the commercial product is yellowish. Its sp. gr. is 1.60 at 15°, but on freezing it contracts 8.3% of its volume. It is slightly volatile; the vapour tension at 70° was found by A. Marshall and G. Peace (*Trans. Chem. Soc.*, 1916, **109**, 298) to be 0.005 cm. of mercury at 70°, which is practically the same as that of mercury. It is not hygroscopic and is almost insoluble in water. It is also insoluble in glycerol and petroleum spirit. It is readily soluble in ether, ethyl acetate, acetone, ethyl and methyl alcohols, chloroform, glacial acetic acid, amyl alcohol, benzene, toluene, nitrobenzene, phenol, olive oil, and sulphuric acid. It dissolves less readily and with partial decomposition in carbon disulphide, nitric acid, and hydrochloric acid (see Elliott, *School of Mines Quarterly*, **4**, 15).

The true freezing-point of nitroglycerin is 13.3°, but that of the commercial product is frequently some degrees lower in consequence of the presence of dinitroglycerin. Nitroglycerin shows the property of supercooling very markedly, and nitroglycerin explosives can often be kept for long periods at temperatures below 0° without freezing.

Solid frozen nitroglycerin is less sensitive to shock than the liquid, but when half frozen it explodes easily, and is consequently very dangerous; moreover, the freezing of the nitroglycerin in composite explosives tends to cause it to separate from the other constituents and form a liquid layer on the surface when it melts again. This phenomenon, known as "exudation," is also a source of danger. To prevent the freezing of the nitroglycerin additions are made of various substances which depress the freezing-point in accordance with van't Hoff's law. Among the substances which have been proposed for this purpose are nitrobenzene, nitronaphthalene, dinitroglycerine, dinitromonochlorhydrin, and nitrates of polymerised glycerol.

Nitroglycerin has a powerful physiological effect. Merely handling it or entering a house containing it will often give a violent headache to anyone not accustomed to it.

Detection.—If some of the dry explosive (1 to 5 grm.) is placed in a dish on a boiling water bath, and the dish is covered over with a glass beaker or funnel, after an hour the glass will be found to be clouded with minute drops of nitroglycerin, if any is present. The appearance is very characteristic, and quite distinct from that of the large drops of liquid which may be formed in consequence of the presence of water or organic solvents.

Nitroglycerin can also be detected by extracting with ether, evaporating off the solvent, and examining the residue. If the residue is a viscous liquid readily soluble in 80% methyl alcohol, but insoluble in water, it is probably nitroglycerin. Absorbed by filter-paper and ignited, it will burn quietly with a peculiar green flame.

Examination.—Nitroglycerin, as such, is not allowed in Britain to be transported out of the factory at which it is made, and for extra security it is usual to mix it, as soon as possible, with guncotton or some other material which renders it less sensitive. Consequently the examination of commercial nitroglycerin is hardly ever carried out, except in the factory.

The percentage of *nitrogen* may be ascertained by weighing out 0.32 to 0.35 grm. into a small beaker, dissolving it in sulphuric acid and introducing it into the Lunge nitrometer, as described above, under Nitrocellulose. The theoretical percentage is 18.53. The results obtained are usually 0.1 to 0.2% lower than this, principally in consequence of the error of the process. If the percentage of nitrogen is very low, it shows the presence of dinitroglycerin or some other impurity.

To determine the alkalinity take 20 grm. shake gently with 50 c.c. of water, and titrate with N/10 sulphuric acid, using methyl-orange as indicator. For nitroglycerin used in the manufacture of cordite, it is specified that the alkalinity shall not exceed 0.005% calculated as sodium carbonate.

Moisture may be estimated by weighing out about 5 grm. into a small dish and allowing it to stand at the ordinary temperature over calcium chloride in a desiccator, which may be evacuated if preferred.

Stability Tests.—The only test usually applied is the Abel heat test, q. v. Guttmann's test cannot be utilised with explosives containing nitroglycerin.

Estimation.—In consequence of the volatility of nitroglycerin it is not practicable to weigh it accurately after extracting it by means of a solvent from a composite explosive. When possible it is therefore estimated by difference, but in many cases it is very desirable to estimate the nitroglycerin directly. If it is known that no other substance is present, which will evolve nitrogen in the nitrometer the percentage of nitroglycerin can be deducted from a nitrogen estimation on the explosive. Or if the amount of nitrogen due to other nitric esters or nitrates is known, it is still possible to calculate the percentage of nitroglycerin. Almost the whole of the ether can be evaporated off from the ether extract of an explosive without incurring an appreciable loss of nitroglycerin, provided it be done at a low temperature. The beaker containing the ether solution is placed on a ground glass plate and covered with a bell jar having two tubulars through which pass glass tubes. A rapid current of air dried by means of sulphuric acid is made to enter through one of these tubes, and is delivered downwards about half an inch above the surface of the ether. The air current is regulated so that a marked dimple is made on the surface of the solution. The air and vapour pass out through the other tube, and may be led out of the laboratory window. The current of air should be passed for about six hours. The nitroglycerin can then be estimated in the residue by means of the nitrometer.

Silberrad, Ablett and Merryman (*J. Soc. Chem. Ind.*, 1906, **25**, 628) have worked out a method for the direct estimation of nitroglycerine which is as follows:

A weighed quantity of the ground cordite, or other explosive sufficient to yield 1.5 grm. of nitroglycerin, is placed in a thimble in the extractor *A* (Fig. 2), which is fitted up as shown. 80 c.c. of absolute ether is poured into the flask and extraction is carried out in the usual manner. After the extraction is complete the thimble containing the nitrocellulose, etc., is washed with a little fresh ether, and removed from the extractor, a little ether being left in the latter. The absorption flasks, *C*, containing 10 c.c. of N/10 acid, are now affixed, and excess of sodium ethylate (about 50 c.c. of a solution prepared by dissolving 5 grm. of sodium in 100 c.c. of absolute alcohol) is run into the flask little by little through the side tube *D*. About 10 c.c.of ethylate solution are also blown up through the stopcock, *E*, into the extractor. The reaction takes place rapidly and is completed by warming on the water-bath for about 6 hours.

The ether is then distilled up into the extractor and run off by means of the tap, and the apparatus is cleansed of vapour by blowing air through. The residue in the flask is dissolved in water and transferred to a 150 c.c. flask, together with the contents of the absorption flask, C, the washings of the flask and extractor are added, and the volume of liquid is made up to the mark. 50 c.c. of the

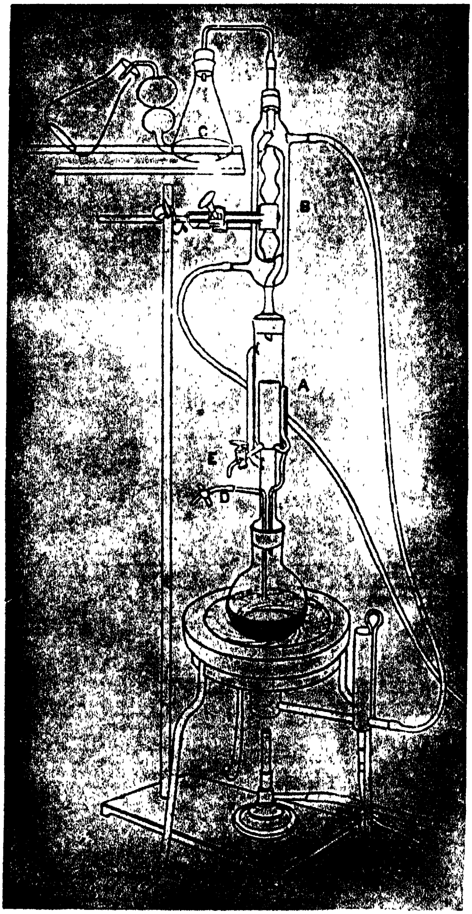

Fig. 25.

solution are then transferred to the flask, F, of the reduction apparatus (Fig. 26), 50 grm of a mixture of powdered zinc (2 parts) and reduced iron (1 part) are added together with 50 c c of 4% sodium hydroxide solution, 60 c.c of N/10 acid being placed in the absorption flasks, H. After the apparatus has stood in the cold for 1 hour, the contents of the flask F are boiled After boiling for 1 hour a current of air is passed through for 1½ hours, boiling being still continued For the last ½ hour there should be no water in the condenser. The excess of standard acid is then titrated back. Each c.c. of N/10 acid corresponds to 0.007567 grm of nitroglycerin. The experimental error does not exceed 1%.

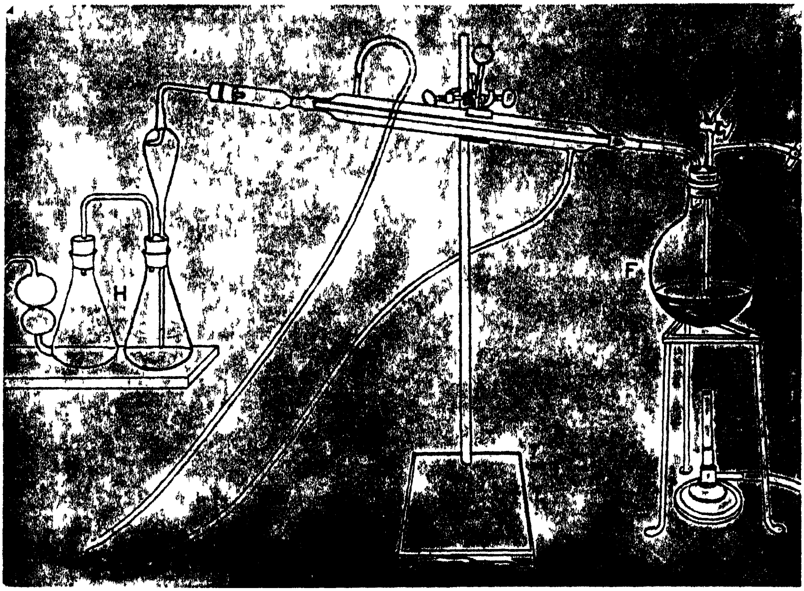

FIG 26

Separation from Nitro-aromatic Compounds.—Many explosives contain nitroglycerin together with a nitro-derivative of an aromatic hydrocarbon, etc. The separate estimation of these substances presents some difficulty, as they are soluble in practically all the same solvents, and nitroglycerin is slightly volatile. If the mixture consist of nitroglycerin and di- or trinitro-toluene, the nitroglycerin can be determined by dissolving in sulphuric acid and shaking up in a nitrometer in the usual way. The di- or tri-nitrotoluene does not interfere with the reaction to an appreciable extent, but if mononitro-toluene be present, it is converted into dinitrotoluene, and the nitrometer reading is correspondingly low.

It has also been proposed to determine the nitroglycerin in these mixtures by the Schultze-Tiemann method, E. Küppers, *Z. ges, Schiess u. Sprengstoffw.*, 1915, **10**, 146 but in this also there is risk of some of the nitric acid set free being taken up by nitro-bodies. A fairly satisfactory gravimetric method has, however, been worked out wherein the nitroglycerin is destroyed by treatment with ferrous chloride in the presence of methyl alcohol, which takes up the nitric acid and so prevents action on the nitro-compounds, which are then extracted with ether and weighed. (W. Dickson and W. C. Easterbrook, *Analyst*, 1922, **47**, 112.)

The ethereal solution of the nitroglycerine and nitro-body obtained by extracting the explosive with pure dry ether is allowed to evaporate spontaneously. The residue is dissolved in 40 c.c. of methyl alcohol and 25 c.c. of saturated ferrous chloride solution are added for every gram of nitroglycerin. 25 c.c. of concentrated hydrochloric acid are also added. The solution is set aside at room temperature for at least 24 hours and then extracted with 3 quantities of ether, 50 c.c. at a time. These are united, washed repeatedly with water until free from iron salts and dried by introducing granular calcium chloride into the separating funnel. The solution is filtered into a large crystallising basin and the calcium chloride and filter are washed with pure dry ether. The ether is allowed to evaporate spontaneously and the residue is washed into a flask with pure dry ether which is again allowed to evaporate off spontaneously, and the residue is dried over sulphuric acid in vacuo and weighed. When the explosive contains substances, such as wood meal, which yield extracts to ether, a suitable correction must be deducted from the weight of nitro-body. The extract is not acted upon by the ferrous chloride solution. The results are correct to within 3% of the nitro-body.

For the estimation of small quantities, such as are used in medicine, Scoville recommends the colorimetric method with phenoldisulphonic acid as used in water analysis. (*Amer. J. Pharm.*, 1911, 359.) An amount of the alcoholic solution of the substance equivalent to about 0.00065 grm. (0.01 grain) of nitroglycerin is allowed to evaporate spontaneously. If tablets are to be examined, five of them are powdered, shaken with 10 c.c. of alcohol for one or two hours, the solution filtered, and 2 c.c. of the filtrate are then treated as above. When dry, 2 c.c. of phenoldisulphonic acid reagent are added, the mixture is well stirred, allowed to stand ten minutes, diluted with water, made slightly alkaline with potassium hydroxide, and diluted to 100 c.c. At the same time an approximately equivalent quantity of a solution containing 0.7215 grm. of potassium nitrate per litre is measured out, evaporated down and treated in the same way, and the colorations, due to the formation of picric acid, are compared. 1.2 c.c. of the standard solution is equivalent to 0.01 grain nitroglycerin.

Other Liquid Nitric Esters.—Several of these have also been used as additions to nitroglycerin in order to make it freeze less readily, and consequently they may be looked for in blasting explosives intended for use in cold climates. Their properties are so similar to those of the nitroglycerin with which they are mixed that they cannot be separated. Dinitroglycerin is one of the substances that have been proposed, but it has never come into use on account of the difficulty of manufacture due to its solubility in water. It sometimes occurs, however, as a natural impurity in ordinary nitroglycerin and then lowers the freezing point. The same applies to tetranitrodiglycerin, but in this case the difficulty lies in making the diglycerin. Dinitro-ethylene glycol (see Naoum, *Z. ges. Schiess u. Sprengstoffw.*, 1920, **15**, 5 and 214; 1922, **17**, 465), has been made and used on a large scale. It is more volatile than nitroglycerin and has a stronger physiological action. Dinitrochlorohydrin is used in Germany to a considerable extent.

To examine for these substances they must be separated together with the nitroglycerin and freed from other material. The examination of the mixture thus obtained will then render it possible to draw conclusions. The mean molecular weight may be determined either from the boiling point of a solution in ether or ethyl acetate, or from the freezing point of a solution in benzene. An estimation of the nitrogen in a nitrometer may also be made. In the case of dinitrochlorohyrdin an estimation of the chlorine will enable one to calculate the quantity present. The following table gives comparative data:

Substance	Formula	Molecular weight	Spec. grav. 15°	Per cent N	B.P. 15 mm.
Nitroglycerin........	$C_3H_5N_3O_9$	227.0	1.601	18.51	160°
Dinitroglycerin......	$C_3H_6N_2O_7$	182 0	1.47	15.38	145
Dinitroglycol........	$C_2H_4N_2O_6$	152 0	1.496	18.43	low
Dinitrochlorohydrin.	$C_3H_5ClN_2O_6$	200.5	1.541	13.91	100
Tetranitrodiglycerin.	$C_6H_{10}N_4O_{13}$	346.0	....	16.19	high

NITRO-COMPOUNDS

A large number of nitro-derivatives of the aromatic series are used both for military high explosives and as ingredients of commercial blasting cartridges. When only one such compound is present there is no great difficulty in identifying it by recrystallising it and taking its melting point. A nitrogen estimation may also be of assistance. When there are two or more, or when the substance is very impure, the problem is of course more difficult, but usually it is possible to separate the constituents in the pure state by repeated crystallisation and then identify them. To ascertain the proportions in which they are present the setting point and nitrogen content of the mixture may be determined. It should be borne in mind, however, that two different mixtures of the same two substances may have the same setting point, but they can be distinguished by adding a little of one of the constituents and seeing whether the melting point goes up or down.

Various precautions are necessary to obtain the true setting point of a mixture, and many of the tables for mixtures of pairs of nitro-compounds that have been published are unreliable through neglect of them. The substance should be dried thoroughly, then melted and poured into a glass tube about 1 in. in diameter, which is placed inside another glass vessel to act as an air bath. This in turn is immersed in a bath of liquid maintained at a temperature about 10° below the setting point. The cooling will then be slow and regular. An accurate thermometer is immersed in the substance which is kept stirred, and the temperature is read at least once a minute and the readings are plotted against the time. At first the temperature falls rapidly to a point below the setting point, then when one of the constituents begins to crystallise out it rises to a maximum, and then falls slowly and regularly. The true setting point is neither the minimum nor the maximum, but is obtained by continuing the straight line of the final cooling to meet the initial curve. (J. N. Bell, and C. H. Herty, *J. Ind. Eng. Chem.*, 1919, **11**, 1124.)

In most cases the fall of the setting point when one nitro-compound is added to another is normal and agrees well with the general equation:

$$\log_e x = -\frac{Q(T_0 - T)}{RTT_0}$$

where x is the molecular proportion of the constituent that crystallises out, Q is its latent heat of fusion, T_0 is its melting point in the pure state on the absolute scale, T the setting point of the mixture and R is the gas constant, 1.985. The complete curve therefore consists of two parts falling from the respective melting points of the two constituents to the eutectic point. The flat portions which were found by Giua were apparently due in most cases to the fact that he took the minimums of the cooling curves as the setting points, and are not sufficient evidence of the formation of molecular compounds, (J. M. Bell and J. P. Sawyer, *J. Ind. Eng. Chem.* (1919), **11**, 1025). The curves therefore are fairly well defined by the eutectic point, the published particulars of which are collected in the following table (see pp. 620 and 621):

Molecular compounds are formed in three of these cases: 2 molecules of trinitrotoluene combine with one of tetryl to form a compound melting at 65° or 68°; T.N.T also combines with nitronaphthalene in molecular proportions, to form a compound melting at about 65°; and 2 molecules of nitrobenzene combine with one of 1:3-dinitrobenzene to form a compound melting at 24°. In these instances of course the setting point curves do not comply with the simple equation given above. By the addition of further substances the setting points can be depressed still more.

The following is a *general test for nitro-compounds:* (S. P. Mulliken, *Identification of Organic Compounds*, Vol. II, 1916, **32**.) Dissolve about 0.2 grm. of the substance in about 3 c.c. of hot 50% alcohol. Add five or six drops of 10% calcium chloride solution and a pinch of zinc dust, and heat until violent boiling begins. Chemical action accompanied by frothing will then often continue for some time without further heating. Allow to stand from 2 to 5 minutes. Filter into a 10% solution of silver nitrate in concentrated ammonia.

TABLE FOR IDENTIFICATION OF MIXED (PAIRS) EXPLOSIVES

Substance A	M. p.	Substance B	M. p.	Eutectic		
				Per cent. A	Set. pt.	Ref.
Hexanitrodiphenylamine	238	2:4:6-Trinitrotoluene	80.6	12	78.2	G269
Picryl sulphide	230.5	2:4:6-Trinitrotoluene	80.6	13.5	78.3	12
1:3:8-Trinitronaphthalene	214	1:2:5-Trinitronaphthalene	114	39	96	13
1:5-Dinitronaphthalene	215	1:8-Dinitronaphthalene	171	22	145	13
Trinitrometaxylene	182	1:8-Dinitronaphthalene	80.5	8	78.4	1
Trinitrometaxylene	182	2:4-Dinitrotoluene	69.5	6	67.7	1
Trinitrometaxylene	182	*p*-Nitrotoluene	51.2	2	50.5	1
Camphor	176	2:4:6-Trinitrotoluene	80.6	43	52	G271
2:4-Dinitrodiphenylamine	157	Diphenylamine	52.5	16	48.5	G323
Dinitronaphthalene	135	Picric acid	122		80	6
Tetryl	127.5	2:4:6-Trinitrotoluene	80.6	33 48	65 65	G268
Tetryl	127.5	2:4:6-Trinitrotoluene	80.6	33 48	68	11
Tetryl	127.5	*p*-Nitrotoluene	53	24	44.4	G268
Picric acid	122	Trinitro-*m*-cresol	107		70	6
Picric acid	121.7	2:4:6-Trinitrotoluene	80.6	33	55.5	G270
Picric acid	119	2:4-Dinitrotoluene	68.8	40	51.6	8
Picric acid	122	1-Nitronaphthalene	61		49	6
2:4:5-Trinitrotoluene	101.5	2:4:6-Trinitrotoluene	80.6	39	58	G264
1:3-Dinitrobenzene	89.4	2:4:6-Trinitrotoluene	80.6	43	51	G203
1:3-Dinitrobenzene	89.4	2:4-Dinitrotoluene	71	43	43	G202
1:3-Dinitrobenzene	89.4	*p*-Nitrotoluene	53	39	30	G201
1:3-Dinitrobenzene	89.4	Nitrobenzene	4	12 42	−2 14	10
2:4:6-Trinitrotoluene	80.6	2:4-Dinitrotoluene	71	46	45	G263 2, 7, 8
2:4:6-Trinitrotoluene	79.4	Nitronaphthalene	55.7	20 73	48 61.5	8

2:4:6-Trinitrotoluene	80.6	2:6-Dinitrotoluene	65	48	37	G262
2:4:6-Trinitrotoluene	80.6	*p*-Nitrotoluene	53	42	34	G261, 2
2:4:6-Trinitrotoluene	80.4	α *o*-Nitrotoluene	−10.4	16	−15.6	3
2:4:6-Trinitrotoluene	80.4	β *o*-Nitrotoluene	− 4.5	19.5	− 9.7	3
2:4-Dinitrotoluene	71	2:6-Dinitrotoluene	65	47	33.6	G262
2:4-Dinitrotoluene	69.8	2:6-Dinitrotoluene	64.7	45	31	5
2:4-Dinitrotoluene	71	*p*-Nitrotoluene	53	47	26.5	G259, 2
2:4-Dinitrotoluene	69.6	*o*-Nitrotoluene	− 4.5	21	−11.5	3
Azobenzene	66.7	Diphenylamine	52.9	40	32	G532
2:6-Dinitrotoluene	65	*p*-Nitrotoluene	53	49	25.5	G260
2:3-Dinitrotoluene	59.2	3:4-Dinitrotoluene	58.4	49	22.5	5
2:3-Dinitrotoluene	59.2	2:5-Dinitrotoluene	50.1	47	19.7	5
3:4-Dinitrotoluene	58.4	2:5-Dinitrotoluene	50.1	43	20.8	5
p-Nitrotoluene	51.3	*m*-Nitrotoluene	15.5	37	− 2.8	4, 5
p-Nitrotoluene	51.5	*o*-Nitrotoluene	− 4	25	15	3, 5, 9
m-Nitrotoluene	15.5	*o*-Nitrotoluene	−10.4	48	−31.6	4

1. J. M. Bell and J. P. Sawyer, *J. Ind. Eng. Chem.*, 1919, **11**, 1025.
2. J. M. Bell and C. H Herty, *J. Ind. Eng. Chem.*, 1919, **11**, 1124.
3. J. M. Bell and others, *J. Ind. Eng. Chem.*, 1921, **13**, 59.
4. J. M. Bell and J. L. McEwen, *J. Ind. Eng. Chem.*, 1922, **14**, 536.
5. W. H. Gibson, R. Duckham and R. Fairbairn, *Trans. Chem. Soc.*, 1922, **121**, 270.
6. C. Girard, *Mon. Sci.*, 1909, 246.
7. F. Langenscheidt, *Z. ges. Schiess-Sprengstoffw.*, 1919, **14**, 66.
8. A. Wogrinz and P. Vari *Z. ges. Schiess-Sprengstoffw.*, 1919, **14**, 268.
9. A. F. Hollemann, *Rec. trav. chim*, 1909, **28**, 408.
10. K. Lehnstedt, *Z. ges. Schiess Sprengstoffw.*, 1918, **13**, 118.
11. C. A. Taylor and W. H. Rinckenback, *J. Ind Eng. Chem.*, 1923, **15**, 73.
12. A. Roche and V. Thomas, *Comptes Rend.*, 1923, **176**, 586.
13. P. Pascal, *Bull. Soc. Chim.*, 1920, **27**, 388. In both these cases there is partial solubility in the solid state. The author gives curves for a number of other mixtures of nitronaphthalenes.

G. M. Giua, *Chimica delle Sostanze esplosive*, 1919, page numbers in the table.

Nitro-compounds thus treated give an immediate black or gray precipitate of metallic silver, or a silver mirror. This test must be accompanied by a blank experiment with an alcoholic solution of the substance and ammoniacal silver nitrate; for it is, of course, useless to apply it to compounds that reduce silver before treatment with zinc dust. A white or light yellow precipitate in the test is without significance.

The usual reduction products of nitro-compounds by the procedure of the test are hydroxylamines. Thus, nitrobenzene gives phenylhydroxylamine, $C_6H_5.NO_2 + 2H_2 = C_6H_5.NH(OH) + H_2O$. The only important classes of nitrogenous carbon compounds not containing the nitro-radical, which, while unable to reduce ammoniacal silver nitrate in the cold, are known to gain the power to do so after the treatment with zinc dust, are nitroso, azo and azoxy substances. Their reduction gives hydroxylamines, hydrazines, or hydrazo compounds. Nitraniline gives aminophenol, which reduces silver solution. The addition of calcium chloride is made to accelerate the reaction.

Nitro-compounds also give with aluminium bromide in benzene solution an orange red coloration which disappears on the addition of water. In the absence of solvent, or in carbon disulphide, no colour is formed in most cases. (S. C. J. Olivier, *Rec. Trav. Chim. Pays Bas* (1918), 241.)

Colour Reactions with Alkalies.—The nitro-compounds can often be detected and even identified by the colour reactions that they give when dissolved in acetone and a little aqueous sodium or potassium hydroxides is added or some alcoholic ammonia. The following table gives the most important of these reactions: (O. Rudolph, *Zeitsch. anal. Chem.*, 1921, **60**, 239; M. Copisarow, *Chem. News*, 1914, 247; E. Calver, *High Explosives*, 1918, 234).

	Alkali hydroxide	Alcoholic ammonia
Nitrobenzene	o	o
o-Dinitrobenzene	Cold o	o
m-Dinitrobenzene	Intense red violet.	o
p-Dinitrobenzene	Intense yellow.	Not distinctive.
1:3:5-Trinitrobenzene	Deep red.	Yellowish red which persists on standing.
o-Nitrotoluene	Light yellow.	Light yellow.
m-Nitrotoluene	Very light yellow.	Very light yellow.
p-Nitrotoluene	o	o
2:4-Dinitrotoluene	Deep blue turning to black and then fading.	o
2:4:6-Trinitrotoluene	Blood red turning to brown.	Red turning to violet.
2:3:4-Trinitrotoluene	Dark green ppt. appears which immediately redissolves and turns black. On warming changes to deep brown. Dilution with water gives red solution.	Gradually changes to brilliant yellow. On warming and dilution no further change.
2:4:5-Trinitrotoluene	Black at first, then violet tinge. On warming again black, then deep brown, which on dilution with water becomes reddish-brown.	Gradually darkens to deep indigo blue. On heating dirty green, then brown. Brown ppt. appears on adding a little water.
3:4:5-Trinitrotoluene	....	Orange red.
2:3:5-Trinitrotoluene	....	Rose red.
α-Nitronaphthalene	Very slight yellowish pink.	o
Dinitronaphthalene	Orange.	Delicate pink.
Trinitronaphthalene	Scarlet.	Orange red.
Tetranitronaphthalene	Orange red.	....
Picric acid	Orange yellow crystals.	The yellow solution becomes slightly reddish.

Nitrogen determinations may be made by the Dumas method which is generally used by the U. S. Bureau of Mines. A number of papers have been published advocating volumetric methods depending upon the reduction of the nitro-groups to amino-groups by means excess of stannous chloride or titanous salts and subsequent titration. The following is the method of Knecht and Hibbert which has been much used:

The standard solution contains about 0.5% of titanium trichloride dissolved in dilute hydrochloric acid, and this is titrated with a standard solution of ferric ammonium sulphate using potassium thiocyanate as indicator. About 0.1 grm. of the nitro-compound is weighed out and dissolved in water, hydrochloric acid or alcohol. In the case of nitro-hydrocarbons and other insoluble substances it is often advisable to sulphonate it first. An excess of the standard titanium solution is added hot, and the whole is boiled for about 10 minutes in an atmosphere of CO_2. The liquid is then cooled and the excess of titanous chloride is titrated with the iron solution. Each $-NO_2$ group takes 6 molecules of titanous chloride: $R.NO_2 + 6TiCl_2 + 6HCl = 6TiCl_4 + R.NH_2 + 2H_2O$. Although this method has given satisfactory results with many materials, *e. g.* picric acid and dinitrochlorobenzene, with others it has yielded low and variable figures.

The matter has been investigated by T. Callan and J. A. R. Henderson who came to the conclusion that error is sometimes introduced by chlorination taking place by the action of the titanium tetrachloride on the nitro-body or the alcohol, and sometimes by loss of the substance through volatilisation with the steam. (*J. Soc. Chem. Ind.*, (1920), **39**, 86T; 1922, **41**, 157T.) They therefore carry out the reaction under an inverted condenser when the substance is at all volatile, and use sulphuric acid instead of hydrochloric, and preferably a solution of titanous sulphate. They prefer to take a larger quantity of the substance and use a stronger solution which is prepared by mixing 400 c.c. of commercial titanous sulphate solution of about 12% strength with 500 c.c. of dilute sulphuric acid (1 in 4), boiling for a few minutes, cooling and making up to 1000 c.c. They standardise it against pure *p*-nitroaniline. This modification of the method is of general application and has been used successfully with nitrobenzene, nitronaphthalene, the nitrotoluenes, nitrochlorobenzenes, nitrophenols, nitrobenzoic acids and trinitrocresol.

Many different variations of the Kjeldahl method have been recommended for various nitro-compounds, but most of them break down with some or other of them, in some cases apparently because of the difficulty of reducing them completely and in others because there is some loss due to volatilisation. B. M. Margosches and W. Kristen found that the Flamand-Prager modification worked well with most of the substances but broke down with *o*- and *m*-nitrotoluene and the corresponding nitrobenzyl chlorides. (*Z. ges. Schiess u. Sprengstoffw.*, 1923, **18**, 39 and 73.) In this method the nitro-body is first reduced with zinc dust and concentrated hydrochloric acid and is then heated in the usual way with sulphuric acid, copper sulphate and potassium sulphate. W. R. Orndorff and R. H. Braden recommend reduction with red phosphorus and hydriodic acid which are more energetic than zinc and hydrochloric acid. (*U. S. Bureau of Mines Bull.*, 1923, **219**, 132.) Weigh out 0.2 to 0.3 grm. of the substance and put it in a 500 c.c. Kjeldahl flask with 0.1 to 0.2 grm. of red phosphorus and 20 c.c. of hydriodic acid of sp. gr. 1.7 (or 27 c.c. of sp. gr. 1.45). If the compound has a high nitrogen content 1 grm. of iodine should also be introduced in order to secure complete reduction. Place the flask in a boiling water bath for 1 hour if the nitrogen content be low, or 1½ hour if it be difficult to reduce like tetryl or teranitroaniline. It is well to agitate the flask several times during this reduction. Then heat the flask carefully for 15 minutes on a small flame so that the contents boil gently. Allow it to cool slightly and add 1 grm. copper sulphate and 45 grm. potassium sulphate. Then cool under running water and meantime pour in slowly 50 c.c. of concentrated sulphuric acid. Shake the flask and then heat carefully with direct flame to drive off the iodine and hydriodic acid. Towards the end of the oxidation use a full flame to drive off all iodine adhering to the neck of the flask. When complete the contents of the flask should be of a clear greenish blue colour. Then distil the ammonia with soda in the usual way. Probably it would be better to carry out the earlier part of the process under an inverted condenser in cases where there is a tendency for the product to volatilise.

PICRIC ACID

$C_6H_2.OH(NO_2)_3$ Mol. wt. 229.1

This substance which is 2:4:6-trinitrophenol is usually made by dissolving phenol in strong sulphuric acid and acting on the resulting phenolsulphonic acid with excess of nitric acid. During the war, in consequence of the scarcity of phenol, large quantities were manufactured from benzene by converting it successively into nitrobenzene chlorobenzene, dinitrochlorobenzene, dinitrophenol and finally picric acid.

Picric acid is not now a constituent of any commercial blasting explosives. Formerly it was used, either alone or mixed with other substances, as a filling for shell by practically all the powers, but now it has been replaced largely by other nitro-compounds, especially trinitrotoluene. The French, still use it under the name of Melinite which, however, often contains other nitro-bodies or paraffin wax to reduce the sensitiveness. Melinite D is simply picric acid, Melinite, O contains also a little trinitrometacresol (Cresilite 2) to reduce the melting point and make it crystallise in a more suitable form. In England poured picric acid is still used largely under the name of Lyddite. Shellite consists of this mixed with dinitrophenol. Blocks of the compressed substance have been used for military demolitions, especially by the Germans under the name of "Sprengmunition 88," but for this purpose also it has been replaced by trinitrotoluene.

Properties.—It forms pale yellow crystalline needles or scales of an intensely bitter taste and sp. gr. 1.767 at 19°. When heated considerably above its melting point in a closed tube it sublimes with decomposition; in the open it burns giving off a very black smoke. As a rule it does not explode under ordinary conditions, but it may be made to do so by dropping it into a red hot tube. If a large quantity catches fire it may ultimately detonate with disastrous consequences. The melting point of the pure substance is 122°.

Picric acid is soluble in about 15 parts of boiling water, but it requires 100 at 15°. The solution is very bitter, bright yellow and reddens litmus. In a stratum 1 in. thick the colour of a solution of 1 part in 30,000 of water is distinctly visible, and is intensified by neutralisation with alkali. A cold saturated solution gives a copious precipitate on adding hydrochloric acid.

It is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, etc.; the last four solutions being colourless or nearly so. Such of the above solvents as are not miscible with water remove picric acid more or less perfectly from its aqueous solution, or that of a picrate which has been freely acidified with sulphuric acid. Ether is preferable to chloroform for this purpose. A solution of picric acid in ether gives up the greater part of its colour to water, but on adding sulphuric acid or, still better, hydrochloric acid, the condition is reversed, the picric acid going chiefly into the ether.

All the above solutions of picric acid, including that in water, dye silk, wool, skin, and other nitrogenous organic matters yellow with a slightly greenish shade. The stain is not removable by water, but soap or alkali partly destroys it. Animal charcoal absorbs a large quantity of picric acid from its aqueous solution.

Detection.—The above mentioned properties of the solutions of picric acid are important indications of its presence. In the presence of other colouring or interfering, the picric acid may be extracted from the aqueous solution by agitation with ether or amyl alcohol, after acidifying strongly with sulphuric acid. The picric acid may then be recovered by evaporating the ethereal solution or agitating it with solution of sodium hydroxide, when it will pass into the alkaline liquid. The extraction of picric acid from an acidified solution by ether, benzene, or amyl alcohol may be made quantitative.

A solution of picric acid is coloured an intense red by potassium cyanide or ammonium sulphide. The reaction with cyanide is very characteristic, but both these colorations are given by trinitro-cresol at once, whereas picric acid only gives them after some time or on heating. These two substances can be distinguished from one another by the fact that potassium picrate is only slightly soluble in cold water, whereas the trinitro-cresylate is readily soluble. If caustic potash be added to a cold saturated solution of picric acid the picrate separates in yellow needles. The pyridine salts behave in the reverse manner.

Picric acid forms highly insoluble compounds with many of the vegetable alkaloids, and the insolubility of the cinchonine salt has been employed for the determination of picric acid. According to Kast picric acid and trinitro-cresol can be detected when diluted with the following quantities of water by means of cinchonine and acridine:

	CINCHONINE	ACRIDINE
Picric acid	5,000	50,000
Trinitro-cresol	17,000	100,000

Of the compounds of picric acid with solid hydrocarbons, that with naphthalene, $C_{10}H_8 + C_6H_2(NO_2)_3OH$, is almost the only one precipitated when the cold alcoholic solution of the hydrocarbon is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of golden-yellow needles, melting at 149°. The formation of naphthalene picrate may be employed to distinguish picric acid from similar nitrocompounds.

Estimation.—A solution of cinchonine sulphate acidulated with sulphuric acid is added to the picric acid solution. The precipitate of cinchonine picrate, $C_{19}H_{22}N_2O(C_6H_3N_3O_7)_2$, is washed with cold water, rinsed off the filter into a porcelain crucible or dish, the water evaporated on the water-bath, and the residual salt weighed. The yellow, intensely bitter alkaloid berberine, is said to precipitate picric acid so perfectly that, on mixing the picric and alkaloidal solutions in equivalent proportions and filtering, the filtrate is colourless and perfectly free from bitter taste.

Acridine has been suggested by Anschütz (*Ber.*, 1884, **17**, 438) as a suitable reagent for the estimation of picric acid, the hydrochloride being used as a precipitant for metallic picrates and a solution of the free base in benzene for the picric acid compounds of hydrocarbons. M. Busch and B. Blume state, however, that the results are inaccurate if the solution be hot, as acridine picrate is decomposed by warm water. They recommend precipitation with nitron, which forms a picrate very insoluble in water and even in 50% alcohol. The solution is precipitated with nitron acetate in a boiling dilute solution acidified with sulphuric acid. The precipitate is filtered off and dried at 110° and weighed. Its weight multiplied by $^{229}/_{541}$ gives the quantity of picric acid. The solution must be free from chlorides, bromides, iodides, perchlorates, nitrates, and chromates (*Z. angew. Chem.*, 1908, 354).

Picric acid may be titrated with standard alkali and phenolphthalein, but according to S. Minovici and C. Kollo excess of alkali is required with lacmoid or phenolphthalein, whereas with Methyl Red (*p*-methyl-amino-azo-benzene-*o*-carboxylic acid) as indicator the colour change is sharp and correct (*Bull. Acad. Sci. Roumaine*, 1914–15, 3, 61). The process is applicable to the ethereal or benzene solution if diluted with alcohol.

Examination.—The melting point requires to be taken with special care as a difference of a few hundredths of a degree may cause the rejection of a large consignment. As the presence of moisture depresses the melting point the material should first be dried for 2 hours in a boiling water oven. The melting point can be taken in the ordinary capillary tube, or the setting point can be taken by melting and then allowing the substance to cool slowly with constant stirring. The temperature at which the thermometer remains steady for a considerable period is the setting point. A low value points to the presence of impurities; these may include dinitrophenol, due to imperfect nitration, or a nitrocresol due to the use of an impure phenol. For filling shell the melting point should not be below 120°.

General impurities and adulterations may be detected and estimated by treating 2 grm. with 50 c.c. of benzene, when any picrates, nitrates, oxalic acid, boric acid, sodium sulphate, alum, sugar, etc. will be left undissolved, and after removal of the liquid may readily identified and determined.

Nitrogen may be determined by the Dumas, Schultze-Tiemann or Kjeldahl-Jodlbauer method, but it is not such a valuable criterion of purity as the melting or setting point.

To test for sulphates, chlorides and oxalates, agitate with cold water from time to time for a few hours. Pour off the liquid and repeat the process if a quantitative determination is to be made. The liquid is concentrated, if necessary, and precipitated in the usual way with barium chloride, silver nitrate or calcium chloride. Free mineral acid may be determined by dissolving in warm benzene, agitating the solution with warm water, removing the benzene layer, and again agitating the aqueous liquid with benzene until the yellow colour is removed and titrating with alkali.

It is necessary to use a solvent when estimating the sulphuric acid or other impurities because portions are liable to be occluded in the crystals and the melting point is too high to release them by melting. T. S. Patterson and K. L. Moudgill prefer to warm 100 grm. of the picric acid with 500 grm. of nitrobenzene in a stoppered bottle at 40°, add 80 c.c. of water, shake, settle and siphon off. This is repeated 3 times, and then the aqueous washings are filtered and the sulphuric acid is precipitated (*J. Soc. Chem. Ind.*, 1923, **42**, 211T).

A method of estimating small proportions of dinitrophenol in picric acid consists in treating the aqueous solution of the sample with bromine, as proposed by A. H. Allen (*J. Soc. Dyers*, etc., **4**, 84). With dinitrophenol the following reaction occurs: $C_6H_3(NO_2)_2OH + Br_2 = HBr + C_6H_2Br(NO_2)_2OH$. With picric acid, bromine reacts as follows: $C_6H_2(NO_2)_3OH + Br_2 + H_2O = HBr + HNO_3 + C_6H_2Br(NO_2)_2OH$. In each case two atoms of bromine enter into the reaction, with formation of a bromodinitrophenol (the same in each case) and one molecule of hydrobromic acid. But in the case of picric acid, nitric acid is formed in addition, and hence the acidity of the liquid at the end of the reaction would be greater the larger the proportion of picric acid present. If the bromodinitrophenol and excess of bromine were removed by agitation with ether or similar solvent, the acidity of the aqueous liquid could be ascertained with great accuracy by titration with standard alkali.[1]

The reaction between bromine and dinitrophenol occurs promptly, but in the case of picric acid it is gradual. In 12 hours it is complete, but in the course of a few minutes there is almost no reaction. This fact enables the reaction with bromine to be utilised for the direct estimation of the dinitrophenol, instead of for its indirect estimation (by estimating the picric acid), as when the acidity is ascertained. The following method of operating was found by Allen to be the most satisfactory: 1 grm. of the sample of picric acid is dissolved in about 100 c.c. of warm water. A saturated solution of bromine in water is diluted with twice its volume of water in a large tapped and stoppered separator, and from this run into a burette. From this burette, a definite volume of the bromine solution, which is approximately of 1% strength, is run into a flask, and an equal volume into another similar flask, both of which are immediately closed. The picric acid solution is then poured into one of the flasks, the last drops rinsed in without delay, and then an excess of a solution of potassium iodide at once added to the contents of both flasks. The liberated iodine is then estimated by titration with a decinormal solution of sodium thiosulphate in the usual way (Allen found iodine to be wholly without action on solutions of either mono-, di-, or trinitrophenol). From the difference in the volume of the solution required in the 2 experiments the amount of bromine which has reacted with the dinitrophenol is easily found. Dinitrophenol reacts with 86.96% of bromine, taking up 43.48%. Mononitrophenol, if present, which is improbable, would react with 230.2% of bromine, taking up 115.1% to form the compound $C_6H_2Br_2(NO_2).OH$. Allen verified these reactions by experiments on specially prepared mono- and dinitrophenol. When the process is applied to commercial picric acid the results are liable to be somewhat in excess of the truth, owing to slight action of the bromine on the picric acid itself.

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[1] (If preferred, before extracting with ether the excess of bromine may be got rid of by adding potassium iodide and then sufficent sodium thiosulphate to react with the iodine liberated.

Commercial picric acid often contains red particles. These have been attributed to the presence of dinitrophenol, but from an observation of T. Whitaker (*J. Soc. Dyers*, 4, 87) it is not improbable that they consist of a nitrosophenol.

PICRATES

At one time many proposals were made to use various salts of picric acid for explosives of all sorts, and such proposals are still made occasionally, but practically no picrates are in use at the present time for this purpose, except in "whistling rockets." Ammonium picrate has been used in conjunction with potassium nitrate as a priming for lyddite shell, but even for this purpose it has been superseded.

Picrates are often formed on plant equipment and articles used in connection with picric acid, and as some of them are sources of considerable danger it is at times necessary to examine for them. They are recognised by their yellow colour and the ordinary reaction of picric acid. Lead picrate is the most dangerous; it is very sensitive to heat, friction and blows and may detonate a large quantity of picric acid if in contact with it. Ferric picrate is also decidedly dangerous. The calcium and magnesium salts are easily ignited and may start a conflagration. The latter are readily soluble in water, but those of iron and lead are only slightly soluble.

2:4 DINITROPHENOL

$C_6H_3OH(NO_2)_2$ Mol. wt. 184.1

This substance is made from dinitrochlorobenzene, as already mentioned. It cannot be manufactured by the nitration of phenol, as it is impracticable to stop the process at this stage. It has been used in Italy, France and England as an addition to picric acid for shell fillings. It reduces the melting point and produces a mixed explosive less sensitive than picric acid alone, principally because it sets in smaller crystals. Dinitrophenol, like other dinitro-compounds, has the grave disadvantage that it is very poisonous to those who handle it.

The m. p. of the pure substance is 114° and that of the material intended either for conversion into picric acid or for use as such should not be lower than 110°. Its properties are similar to those of picric acid, but it is not so sensitive nor such a powerful explosive, and it has not such a great tendency to form salts, but it is an explosive and has caused at least one serious explosion. For its estimation in the presence of picric acid see above under picric acid. It contains 15.23% of nitrogen.

The Derrien test applied at frequent intervals in France to the urine of those who work with this substance is as follows: 10 c.c. of the urine are mixed with 1 c.c. of 10% sulphuric acid and 10 drops of a 1% solution of sodium nitrite, shaken and left in the dark for 5 minutes. Then 2 c.c. of a saturated solution of β-naphthol in ammonia are added and the liquid is allowed to stand for 2 minutes, after which it is shaken with 10 c.c. of ether. A pink colour means a positive reaction, and if the depth of colour exceeds a limit the man is withdrawn from the work.

2:4:6-TRINITROCRESOL

$C_6H.CH_3.OH.(NO_2)_3$ Mol. wt. 243.1

This substance is made by nitrating *m*-cresol, which is the only cresol that gives a satisfactory yield of the trinitroderivative. The melting point of the pure substance is about 107°, but the commercial product is generally rather impure and therefore melts some degrees lower. It has been used on a considerable scale as a constituent of cresilite and other shell fillings. Its properties resemble those of picric acid (*q. v.*). It contains 17.29% nitrogen.

2:4:6-TRINITROANISOLE

$C_6H_2.OCH_3.(NO_2)_3$ Mol. wt. 243.1

This is made by treating dinitrochlorobenzene with sodium methoxide and then nitrating. It also has been used in shell fillings, but its m. p., 69°, is inconveniently low and it has an injurious action on the skin. It is readily hydrolysed to picric acid and then may form sensitive picrates.

NITROBENZENES

Mononitrobenzene, $C_6H_5NO_2$, mol. wt. 123.1, is a liquid at the ordinary temperature and boils at about 210° under a pressure of 760 mm.; it has a vapour pressure of 1 mm. at 53°. It is sometimes used in small proportion in smokeless powders to harden the grains, and also in Sprengel explosives to mix with potassium chlorate just before use. For ordinary blasting explosives it is unsuitable on account of its volatility. It is recognised by its characteristic smell. It contains 11.38% N. It cannot be detonated and therefore is not to be considered an explosive by itself.

***m*-Dinitrobenzene,** $C_6H_4(NO_2)_2$, mol. wt. 168.1, is made by the nitration of benzene and is liable to be contaminated with small quantities of the other two isomers as well as mono and tri-nitrobenzene, etc. The pure substance melts at 89.7° and boils unchanged at 297°. It contains 16.66% N. It can be detonated alone, although only with difficulty, and then goes off with great violence. In conjunction with ammonium nitrate or other oxidising salts it forms a constituent of a number of commercial blasting explosives, in spite of its poisonous properties. The Germans during the war used it in shell fillings.

It may be identified by reduction to *m*-nitroaniline, which forms orange yellow needles melting at about 113° uncorrected (S. P. Mulliken, *Identification of Organic Compounds*, Vol. II, 245). Dissolve 0.1 grm. in 10 c.c. of 96% alcohol, add 1 c.c. ammonia (sp. gr. 0.90) and pass H_2S for 5 minutes into the solution heated nearly to boiling. Distil in a small flask until reduced to 1 c.c., acidify with HCl, add 1 c.c. water, filter and make the filtrate alkaline with sodium carbonate solution. Filter, wash the precipitate with cold water and dissolve in 2 c.c. of boiling water. Filter hot and shake persistently while cooling. Filter and repeat the crystallisation from water. Dry for 10 minutes on a tile at 100° and take the m. p.

For the detection of *m*-dinitrobenzene in the urine of workers with the substance F. Koelsch reduces more drastically in order to convert it into *m*-phenylenediamine (*Zentr. Gewerbehygiene*, 1918, 195). He shakes the urine for a considerable time with zinc dust and strong hydrochloric acid, filters, renders alkaline with sodium hydroxide, extracts with ether or chloroform and evaporates the solvent. The diamine thus obtained is dissolved in water and treated with a fresh warm mixture of sodium nitrite and acetic or hydrochloric acid, whereby it is converted into Bismark brown (phenylene brown). In the most acute cases of poisoning, however, the urine often gives a negative reaction, presumably because the substance is either absorbed by the organs or converted into some derivative that does not give the test.

Trinitrobenzene is a very good high explosive, but it is not used because it is too difficult and expensive to manufacture.

NITROTOLUENES

These substances are used more extensively in explosives than any other nitro-derivatives. Before the war they were already made in Germany on a large scale, and during it the manufacture was developed in England to a very high state of technical efficiency (Sec *Technical Records of Explosives Supply*, No. 2, *H. M. Stationery Office*, 1920).

The **mono-nitrotoluenes,** $C_6H_4.CH_3.NO_2$, mol. wt. 137.1, have been used as an addition to nitroglycerin explosives in order to depress the freezing point and also to assist the gelatinisation of the nitrocotton. They are distinctly volatile at the temperature of the water bath. The composition of the crude product can be ascertained from the setting points before and after the addition of more of one or more of the constituents (W. H. Gibson, R. Duckham, and R. Fairbairn, *Trans. Chem. Soc.* 1922, **121**, 270). That obtained in the usual way by the nitration of technically pure toluene has a setting point of about 30° and a second setting point at about −17° and contains the 3 isomers in the proportions:

ortho	61.0–63.0%
para	32.0–33.5
meta	4.2– 4.5

The presence of dinitrotoluene and impurities derived from the toluene such as nitrobenzene will of course depress the setting points. As there is a larger demand for the para-compound for the manufacture of dyes, the ortho or crude mixtures consisting largely of it, may be found in commercial explosives. Or they may be further nitrated.

The **dinitrotoluenes,** $C_6H_3.CH_3.(NO_2)_2$, mol. wt. 182.1, are to be found in many commercial mixed blasting explosives and also occasionally in smokeless powders. According to Gibson and his co-workers the direct nitration of toluene gives a mixture setting at 56° containing the various isomers in the following proportions:

Isomer	Proportion	Melting Point	
		Giua	Gibson
2:4	74.8	71.0°	69.8°
2:6	20.7	65.5	64.6
3:4	2.5	60.0	58.4
2:3	1.1	63.0	59.1
2:5	0.9	52.5	50.1
3:5	0	91.0	

Paranitrotoluene gives the 2:4-compound only, and *m*-nitrotoluene 67% 2:4 and 33% 2:6. Different workers have given somewhat divergent figures for the m.p.s.; the above table contains those of Gibson and his co-workers (*loc. cit.*) and Giua (*Chimica Selle Sostanze esplosive,* 1919, pp. 226, 227). W. Rintoul (*J. Soc. Chem. Ind.*, 1915, **34,** 60) from a very thorough investigation of the m. p. of the 2:4-derivative gave it as 69.9 to 70.2°. For the manufacture of smokeless powder a purified 2:4-dinitrotoluene is used setting not lower than 65.5°. The volatile matter lost at 60° should not exceed 0.25%, the residue on ignition should not be more than 0.05%, the matter insoluble in benzene 0.1% nor the acidity 0.005% calculated as H_2SO_4. For blasting explosives containing an absorbent material such as wood meal, or in which the nitro-compound is stiffened by the addition of nitro-cotton, a product of lower setting point may be used as there is then no danger of the impurities exuding out. In fact, by-products from the purification of nitro-toluenes are in use under the names of "liquid dinitrotoluene" and "liquid trinitro-toluene" which only set at low temperature. These are complex mixtures consisting mainly of a mixture of dinitrotoluenes. They are generally gelatinised by means of about 4% nitrocellulose. A liquid dinitrotoluene of English origin examined by Kast contained 14.8% N, whilst "liquid trinitrotoluenes" from the same source had 15.5 to 15.65%, whereas the pure trinitro-compound contains 18.50 and dinitrotoluene 15.39% N.

The 2:4-compound may be recognised by reduction to 2:4-tolylene diamine (S. P. Mulliken, *Identification of Organic Compounds*, Vol. II, 1916, 169). Place 0.2 grm. in a large test tube, add 1.5 grm. granulated tin and 2 c.c. hydrochloric acid (sp. gr. 1.2), and heat sufficiently to melt the substance and maintain a moderate action, adding more tin if necessary, until all oily drops disappear. Cool and add 10 c.c. KOH solution (1.2). After cooling shake with 10 c.c. ether, pipette off the ether and evaporate it on the water bath, dissolve the residue in 15 c.c. of hot ligroin and filter hot. Separate the crystals that form on cooling and wash them with 5 c.c. of cold ligroin and dry them on a tile at about 75°. 2:4-tolylene diamine forms long slightly coloured needles melting at 99° (uncorrected).

The 2:6-compound on reduction with boiling alcoholic ammonium sulphide gives pale yellow 6-nitro-*o*-toluidine, melting at 91.5°, whilst the 2:5 under the same conditions yields saffron yellow 6-nitro-*m*-toluidine, m. p. 138°.

2:4:6-Trinitrotoluene, $C_6H_2.CH_3.(NO_2)_3$, mol. wt. 227.1, was used more largely during the war than any other nitro high explosive, especially by England and Germany, and is generally called trotyl or T.N.T. It is also a constituent of many commercial blasting explosives. Both 2:4 and 2:6-dinitrotoluene yield this substance only on further nitration, and consequently toluene on complete nitration gives 95.5% of it, and only 4.5% of unsymmetrical T.N.T.s derived from *m*-nitrotoluene. (Gibson and others, *loc. cit.*) The composition is:

		M. P.
α or 2:4:6–T.N.T.	95.5%	80.8°
γ 2:4:5	2.9	104
β 2:3:4	1.3	112
φ 2:3:6	0.3	111

This mixture has a setting point of 78.4°, and that actually obtained on a large scale by a two-stage nitration process without any intermediate purification had an average setting point of about 76.5°. This contained, of course, some dinitrotoluene and other impurities. This was the method of manufacture adopted in England during the war, but under peace conditions it is more usual to nitrate first to mono-, then to di-, and finally to trinitrotoluene, separating some of the isomers for the manufacture of dyes. For the manufacture of some explosives a product having a setting point of 76° is good enough, but when there is danger of the oily impurities exuding it is necessary to purify it either by recrystallisation from a mixture of benzene and alcohol, or by washing with cold alcohol or by treating it with an aqueous solution of sodium sulphite, which attacks and dissolves the unsymmetrical T.N.T.s and raises the setting point by about 2.2°. (*Technical Records of Explosives Supply No. 2*, 1920, 97.)

2:4:6-Trinitrotoluene is a crystalline substance of pale yellow colour, almost white when pure and melting at 80.8°. With ammonia dissolved in alcohol or acetone it gives a characteristic red coloration turning to violet. When boiled with aniline dissolved in petroleum spirit 2:4:6:-trinitrotoluene forms an addition compound melting at 84°. The solubilities in various solvents over wide ranges of temperature have been determined by C. A. Taylor and W. H. Rinkenbach (*J. Amer. Chem. Soc.*, 1923, **45**, 44). The following table gives the number of grams dissolved by 100 grm. of solvent at 15°:

Water	0.012	
Carbon disulphide	0.35	
Carbon tetrachloride	0.50	
Alcohol (95%)	1.07	
Ether	2.85	
Aniline	7.4	
Chloroform	15	
Toluene	45	
Benzene	50	
Acetone	92	
Pyridine	137	at 20°

Detection in Urine.—Trotyl does not pass through the system unchanged after absorption through the skin of the worker, but is reduced, probably in the liver, to 2:6-dinitro-4-hydroxylaminotoluene (T. A. Webster and G. A. Wyon, National Health Insurance, Medical Research Committee, Special Report Series, No. 11, 1917,

20) and is excreted in the urine combined with glycuronic acid. This gives the same colour reaction with alkali as trotyl itself, but in order to eliminate other colouring matters which may mask the reaction "Webster's test" is applied: 12.5 c.c. of the urine are mixed with 12.5 c.c. of sulphuric acid (20%) by volume and the mixture is shaken with ether. The extract is washed with water, tap water (C. Voegtlin, C. W. Hooper and J. M. Johnson, *U. S. Hygienic Laboratory Bull.*, 1920, **126**, 49) or dilute sodium carbonate solution (F. Tutin, *Physiol. Abstr.*, 1918, **3**, 452) and then 5 c.c. of a 5% solution of caustic potash in absolute alcohol is added. When T.N.T. is present a purple coloration is developed at once varying according to the amount from a faint trace to deep purple. The quantity can be estimated roughly either from the depth of the tint or rapidity with which it changes to brown. As the urine may be contaminated with T.N.T. which has not passed through the system it is often advisable to extract it first of all with ether, which removes this but not the glycuronate of the derivative.

This test, however, has not been found to be of much use in searching for workers who are constitutionally unsuited to work with trotyl, as the suitable men also eliminate the substance in their urine, and in America it was found that observation of the colour of the urine itself afforded more guidance (G. R. Minot, *J. Indust. Hyg.*, **1**, 1919–20, 301; A. Hamilton, *J. Indust. Hyg.*, 1921, **3**, 114). With workers who were being affected injuriously by the T.N.T. the urine was brown to black. It does, however, make it possible to eliminate the workers who absorb abnormal amounts of T.N.T. It may be said generally that the principal protective measures for the worker are personal cleanliness and abstention from alcohol.

Estimation.—To estimate trotyl in admixture with tetryl C. A. Taylor and W. R. Rinkenbach take advantage of the fact that 100 grm. of carbon tetrachloride at 0.5° dissolve 0.215 grm. of the former and only 0.0073 grm. of the latter at 0.3° (*J. Ind. Eng. Chem.*, 1923, **15**, 280). 0.3 grm. of the mixture is heated with 100 c.c. of carbon tetrachoride. The flask is stoppered and allowed to cool and and is then immersed in ice for 4 hours with intermittent shaking. Whilst the contents are at 0–0.5° some of the supernatant liquid is drawn off, weighed, evaporated in a current of dry air, and the residue is dried to constant weight at 60° and weighed. The result is corrected for the solubility of tetryl and is accurate to within about 2%, the error increasing with the per cent. of trotyl.

For rapid works control of such simple mixtures as amatol E. W. S. Colver treats 50 or 100 grm. with hot dilute mineral acid in order to dissolve the ammonium nitrate or other soluble oxidising agent and melt the amatol, which is then measured in a special graduated tube (High Explosives (1918), 237). The density of melted trotyl at 95° is about 1.45, but it is better to standardise the method and tube by means of samples carefully analysed by extraction with benzene.

To ascertain the thoroughness of the mixing of amatol E. P. Perman weighs out a number of portions of 1 mgr. each and estimates the ammonium nitrate in each by means of Nessler solution using a tintometer and a pointolite (*J. Soc. Chem. Ind.*, 1922, 41, 155T.).

Examination.—The determination of the setting point is most important in the case of trotyl that is to be used for filling shell, especially if the mixed explosive is to contain a large proportion of the trotyl or the shell, are to be sent to hot climates, because the liability to exude oil increases rapidly as the setting point falls. In England 3 grades of trotyl have been recognised officially, the lower limits for which are: grade 1, 180.0°, grade 2, 279.5°, grade 3, 376.0°. The material for the test should be dried thoroughly by heating for 2 hours at 90° and then allowed to cool slowly as already described. For routine tests when the drying would occupy too much time the "wet setting point" is sometimes taken with the trotyl mixed with an excess of water. By adding 3.7° to the wet setting point the dry setting point is obtained.

Another objection to the presence of unsymmetrical T.N.T.s in the material is that they are liable to react with impurities in ammonium nitrate, with evolution of gas, which drives out the exudation and sets up pressure in the shell. Trotyl is also liable to contain small quantities of dinitrotoluene, nitrobenzoic acids, nitrocresols and tetranitromethane. To a large extent these are due to the oxidation of the derivatives of *m*-nitrotoluene which are not readily nitrated to the tri-stage. They all depress the setting point. Tetranitromethane being volatile (b. p. 126°) is largely but not entirely removed in the steaming process. It may be recognised by its suffocating smell.

The moisture should be estimated by the dish and cone method (Fig. 4) as trotyl is slightly volatile. For making hot mixed 40/60 amatol it is desirable to keep it down to 0.1%. The organic matter insoluble in benzene should not exceed 0.1%. The ash may be estimated by incinerating this residue, or directly by igniting 5 grm. in a platinum crucible with a little sulphuric acid. It should not exceed 0.05%, and there is little difficulty in attaining this, as the mineral impurities settle out during the hot washing process. The washing also removes the mineral acid which should be undetectable with litmus paper.

2:4:6-TRINITRO *m*-XYLENE

$(CH_3)_2C_6H(NO_2)_3$ Mol. wt. 241.1

This substance has been used to some extent as a filling for shell and as a constituent of commercial blasting explosives. It is made by nitrating commercial xylene and is not pure, as this contains *o*- and *p*-xylene as well as the *m*-compound. These are not so readily nitrated as *m*-xylene, with the result that dinitroxylenes are also present. The high melting point, 182°, is also an obstacle both in manufacture and use, and consequently this compound is often mixed with trotyl (See J. Marshall, *G. Ind. Eng. Chem.*, 1920, **12,** 248).

NITROCHLOROBENZENES

Although many of these substances are comparatively easy to manufacture and are powerful and violent explosives, they have not been used much for this purpose because they are very poisonous and are liable to be converted by moisture into nitrophenols which form sensitive salts. Also, in many cases the melting points are inconveniently high or low.

2:4-Dinitrochlorobenzene, $C_6H_3Cl.(NO_2)_2$, mol. wt. 202.5, has been made on a considerable scale as an intermediate in the manufacture of picric acid and hexanitrodiphenylamine. It is a crystalline substance melting at 50°.

Crude dinitrodichlorobenzene was used in the United States during the war as a high explosive under the name of "Parazol." It was made by nitrating *m*-dichlorobenzene. It contained all the three possible isomers, namely:

2:5-dinitro-1:4-dichlorobenzene	m. p. 81°
2:3-dinitro-1:4-dichlorobenzene	m. p. 103°
2:6-dinitro-1:4-dichlorobenzene	m. p. 106°

of which the first predominated (E. H. Nason, *J. Amer. Chem. Soc.*, 1918, **40**, 1602). The 2:6-compound gives an intense cherry red coloration with caustic soda in acetone solution, a dark reddish brown with alcoholic ammonium sulphide, and an intense red with alcoholic potassium cyanide. The 2:3-compound gives orange with sodium hydroxide in acetone, yellow with alcoholic ammonium sulphide and light yellow with alcoholic potassium cyanide. (C Voegtlin, A. E. Livingston and C. W. Hooper, *U. S. Public Health Service, Hygienic Laboratory, Bull.*, 1920, **126**, 183.) The crude mixture is a coarse, sticky, yellow powder with a pungent odour and a setting point of about 60°. In addition to the above 3 isomers it contains some *p*-nitrochlorobezene (m. p. 83°). It is soluble in the usual organic solvents.

NITRONAPHTHALENES

Mono-, di- and trinitronaphthalenes are used sometimes as constituents of shell fillings and extensively in blasting explosives, especially in France and Belgium. Crude products are generally employed containing various isomers of differing degrees of nitration.

α-Nitronaphthalene, $C_{10}H_7.NO_2$, mol. wt. 173.1, is a light yellow crystalline substance melting, when pure, at 61°, but the technical product generally has a setting point of about 56°. By itself it is inexplosive, as would be expected from the fact that it contains only 8.09% N. The β-compound is not formed in the nitration of naphthalene. It gives practically no coloration with either alcoholic ammonia or soda, but when a little is added to a mixture of equal volumes of sulphuric acid and water a brilliant red colour is produced. It is very soluble in alcohol and ether.

Dinitronaphthalene, $C_{10}H_6.(NO_2)_2$, mol. wt. 218.1. The two principal isomers formed in the nitration of naphthalene or nitronaphthalene are the 1:5 and 1:8-compounds melting, respectively, at 217° and 170°. The technical product is a greyish white powder with a setting point usually between 138° and 155°. It is only slightly soluble in alcohol and ether, but readily in benzene, xylene, glacial acetic acid, turpentine and acetone. When heated slowly it decomposes at 318° with evolution of gas. It gives a delicate pink coloration with alcoholic ammonia, and orange with caustic soda. It contains 12.84% N.

Trinitronaphthalene, $C_{10}H_5.(NO_2)_3$, mol. wt. 263.1. The commercial product consists mainly of the 1:3:8-compound (m. p. 214°) with some 1:2:5 (m. p. 114°), 1:3:5 (m. p. 126°) and 1:4:5 (m. p. 147.5°) (Pascal, *Bull. Soc. Chim.*, iv, 1920, **27**, 388). The mixture usually melts at about 110°. The pure compounds contain 15.97% N.

Tetranitronaphthalene requires such a large expenditure of acid for its manufacture that it is seldom made.

TETRYL

$(NO_2)_3.C_6H_2.N\begin{smallmatrix}\diagup NO_2 \\ \diagdown CH_3\end{smallmatrix}$ Mol. wt. 287.1

This substance, tetranitromethylaniline, or more correctly 2:4:6-trinitrophenylmethylnitroamine, is made by nitrating dimethylaniline. It is a powerful and violent explosive, more sensitive than either trotyl or picric acid, and has therefore been used largely as an intermediate or "booster" charge to transmit the comparatively feeble explosion of a detonator to an insensitive explosive such as trotyl or amatol. It has also been used as a constituent of blasting explosives, but not on a large scale because it is somewhat expensive. It is a crystalline substance of faint yellow colour, melting at 129°, readily soluble in acetone and nitric acid, slightly in alcohol, chloroform and ether, and almost insoluble in carbon disulphide, carbon tetrachloride and water (C. A. Taylor and W. H. Rinkenbach, *J. Amer. Chem. Soc.*, 1923, **45**, 104). The pure material contains 24.40% N.

The commercial product is usually of a high degree of purity. The melting point should not be below 128° or even 128.5°; it should be determined on a portion of the material which has been dried thoroughly by heating it a few degrees above the melting point. As tetryl is very slightly soluble in water and has an acid reaction there is some difficulty in estimating the amount of mineral acid present as impurity. The best method is to dissolve 10 grm. in 100 c.c. of benzene, shake out with water and titrate with standard alkali: the amount should not exceed 0.08% calculated as HNO_3. If the tetryl has been purified by solution in acetone or nitric acid and precipitation with water, the matter insoluble in acetone should not exceed 0.05%, of which not more than 0.03 should be organic, but if the purification has consisted merely of boiling with water, these figures may be as high as 0.3 and 0.25%. The moisture as estimated by heating in a boiling water bath for some hours should not be more than 0.05%. Sometimes tetryl is corned by adding about 1% of gum dissolved in alcohol and passing the paste through a sieve and drying. As the gum is insoluble in acetone, this process naturally affects the test for matter insoluble in this solvent. When boiled with caustic alkalies tetryl is converted into picric acid and methylamine.

2:3:4:6-TETRANITROANILINE

$NH_2.C_6H.(NO_2)_4$ Mol. wt. 273.1

This substance, which is made by nitrating *m*-nitroaniline, has been strongly advocated as a substitute for tetryl by its discoverer B. Flürscheim, but hitherto it has not been used on a large scale. It is a very powerful and violent explosive and fairly stable. When boiled with water it is converted into trinitro-*m*-aminophenol (m. p. 174–175°), and the same substance is obtained in the cold by the action of an aqueous solution of sodium acetate. It is also attacked by ethyl and methyl alcohols. It is a yellow crystalline substance melting with decomposition at 210 to 216°; it explodes at 220 to 233°. Its absolute density is 1.89 (B. Flürscheim, *J. Soc. Chem. Ind.*, 40, 1921, 47 T), but when compressed ino pellets these have a density of about 1.68 which is the same as tetryl has under the same conditions. (H. Kast, *Spreng- und Zündstoffe*, 1921, 277.)

2:4:6:2′:4′:6′-HEXANITRODIPHENYLAMINE

$(NO_2)_3.C_6H_2.NH.C_6H_2.(NO_2)_3$ Mol. wt. 439.3

This substance, which is also called scientifically dipicrylamine and commercially hexamine or hexyl, was used on a considerable scale during the war by the Germans for filling torpedoes and air-bombs in conjunction with trotyl. When melted with trotyl it forms a pasty mass which can be cast into any hollow vessel and sets only a few degrees below the setting point of trotyl. Such castings have a suitable degree of sensitiveness and a high density of 1.64 to 1.70, and detonate with astonishing violence. When detonated under water such mixtures are much more effective than trotyl alone, and it is stated that a single charge will sink a ship for which several charges of other high explosives would be required. (A. Stettbacher, *Schiess und Sprengstoffe*, 1919, 205.) These advantages compensate for the comparatively high cost of production.

It can be made by the direct nitration of diphenylamine, but only with difficulty, and it is better made by condensing dinitrochlorobenzene with aniline and then nitrating in two stages with nitric acid of sp. grs. 1.34 and 1.50 respectively. Mixed acid is not used because the intermediate products are insoluble in sulphuric acid. It is a yellow crystalline powder having a melting point of about 238° when crude, and 249° with decomposition when recrystallised. It is only slightly soluble in most organic solvents, but acetone dissolves it rather better, and glacial acetic and nitric acid fairly well. Nitrobenzene and nitrotoluene are, however, the best solvents. It has decided acid properties, but does not form salts so readily as picric acid because it is almost insoluble in water, nor are they so sensitive when formed. The ammonium salt has been used as a yellow dye under the name of aurantia.

Hexanitrodiphenylamine turns the skin a brownish red and with some individuals causes troublesome blisters.

PICRYL SULPHIDE

$(NO_2)_3.C_6H_2.S.C_6H_2.(NO_2)_3$ Mol. wt. 456.2

This compound is similar in constitution and explosive properties to the last and was used by the Germans for the same purpose. It is made by the action of one mol. of sodium thiosulphate on two of picryl chloride in the presence of magnesium carbonate to neutralise the sulphuric acid that is formed. (Germ. Pat. 275, 037.) It is a golden yellow crystalline substance which melts at 233–234° (corrected) when pure, and has no odour. It is only slightly soluble in alcohol and ether, but readily in acetone and glacial acetic acid. (C. F. Van Duin and B. C. R. Van Lennep, *Rec. trav. chim.*, **39**, 1920, 145.)

Other diphenyl compounds have been proposed such as picryl sulphone, (Germ. Pat. 269, 826: van Duin and van Lennep, *loc. cit.*) hexanitrodiphenyl (Germ. Pat. 286, 736: van Duin and van Lennep, *loc. cit.*) and 2:4:6:3′:4′:6′-diphenyl ether, (Germ. Pat. 281, 035, van Duin and van Lennep, *loc. cit.*), but they have not been used on account of the expense of manufacture or the sensitiveness of the explosives.

FULMINATE OF MERCURY

$Hg(ONC)_2$ Mol. wt. 284.6

This substance is made by dissolving mercury in nitric acid and adding alcohol to the liquid. It is readily fired by a blow, by friction or by heat, and then detonates with some violence. It is therefore used for filling detonators and is a component of most cap compositions. It is of course somewhat expensive and not a very powerful explosive: therefore it is not used for other purposes.

Pure fulminate is white, but the commercial product is usually grey or brownish due to traces of resinous matter formed in the reaction. If during manufacture a small proportion of copper and hydrochloric acid be added to the nitric acid solution just before it is poured into the alcohol, white fulminate is obtained, but analysis shows that it contains more instead of less impurity than the grey variety. The whiteness is apparently due to the bleaching of the impurities and not to their elimination.

To the naked eye fulminate looks like fine sand; under the microscope it is seen to consist of crystals generally 0.01 to 0.1 mm. long. They are octohedra, usually truncated, only the smaller crystals being fully developed. The sp. gr. is 4.42 or 4.39, but when merely shaken down the apparent density is only about 1.75. In detonators it is usually compressed to a density of about 2.5. A litre of water dissolves 0.7 grm. at 13°, 1.7 at 49° and about 8 grm. at 100°. In alcohol it is not much more soluble. It is only slightly soluble in acetone and ethyl acetate and is practically insoluble in benzine, glycerin, linseed oil, turpentine and ethyl nitrate. (A. Langhans, *Z. ges. Schiess u. Sprengstoffw.*, 1920, **15**, 219, 227 and 235.) 100 c.c. of boiling chloroform 0.0066 grm. (A. Marqueyrol and Phoriette, *Mem. Poudres*, 1921, **18**, 94.) From water it is said to crystallize with half a molecule of water in small fibrous crystals. Mercury fulminate dissolves readily in an aqueous solution of potassium cyanide, from which it can be reprecipitated with strong acid; pyridine also dissolves it easily, and it can be recovered from the solution again by pouring into water. R. Philip, however, found that the best method for purifying small quantities in the laboratory is to dissolve it in ammonia, filter rapidly, and neutralise with 30% acetic acid. Fulminate is also soluble in solutions of thiosulphate, especially if acid be added, but it is decomposed thereby. Concentrated hydrochloric acid also dissolves it with decomposition.

The residue left when the substance is dissolved in any of these solvents should be small, and when examined under the microscope this residue should be free from particles of metallic mercury. The fulminate should be free from oxalates and chlorides.

It gives a characteristic reaction with phenyl hydrazine. (A. Langhans, *Z. angew. Chem.*, 1918, **31**, 161.) If 0.2 to 0.3 grm. be placed in a test tube with ½ to 1 c.c. of phenyl hydrazine at the ordinary temperature, the fulminate, if present, is coloured first olive green and then grey, until after some hours no fulminate remains. The reaction takes place more quickly at a higher temperature, the colour becoming in turn olive green, grey, brown, reddish brown and finally dark red, with the evolution of nitrogen and combustible gas and the formation of globules of mercury. Strong acid favours the reaction, but alkali prevents it. Fresh solutions in sodium thiosulphate and pyridine give it.

Brownsdon pointed out that when fulminate is treated with a solution of sodium thiosulphate it dissolves with formation of alkali, and the fulminate can be determined by titration with standard acid. This reaction has been investigated by Philip, and by G. Peace and myself. The results are in agreement with the equation:

$$Hg(CNO)_2 + 2Na_2S_2O_3 + 2H_2O = HgS_4O_6 + C_2N_2 + 4NaOH.$$

The cyanogen, of course, reacts with the caustic soda to form cyanide and cyanate:

$$C_2N_2 + 2NaOH = NaCN + NaCNO + H_2O$$

but on adding acid cyanogen is regenerated:

$$NaCN + NaCNO + H_2SO_4 = C_2N_2 + Na_2SO_4 + H_2O.$$

If the alkaline solution be allowed to stand, the alkalinity gradually diminishes, due to the formation of sulphate and thiocyanate from the tetrathionate, cyanide and cyanate:

$$HgS_4O_6 + NaCN + NaOCN + 2NaOH = HgSO_4 + Na_2SO_4 + 2NaSCN + H_2O.$$

This secondary change is restrained by a large excess of thiosulphate, but more effectively by potassium iodide. In the absence of iodide and with only a moderate excess of thiosulphate half the alkalinity disappears in about one hundred minutes at 30°, and practically the whole of it in twenty-four hours. With ten times as much potassium iodide as fulminate of mercury in the solution only 12 % of the alkalinity disappears in one hundred minutes, and if the titration be carried out at once, the loss is quite small. If the fulminate be dissolved with excess of the iodide and a known volume of standard thiosulphate, the excess of thiosulphate can also be titrated with standard iodine solution after the alkali has been neutralised with standard acid, and so a double estimation is effected on the same quantity of material. To this Philip has given the name of the "Bofors method;" it is carried out as follows:

50 c.c. of N/10 thiosulphate solution are pipetted into a beaker, and about 3 grm. of pure potassium iodide are dissolved in it; 0.3 grm. of the fulminate is rapidly washed in and the liquid is agitated until it is dissolved. The fulminate may be moistened beforehand with alcohol to prevent particles floating on the surface or forming lumps. A few drops of Methyl Orange solution are now added and the solution is titrated with N/10 sulphuric acid; then a little starch solution is added and it is titrated with N/10 iodine solution. The whole operation can be carried out in six minutes. The solutions may be standardised either by the ordinary methods, or upon fulminate of mercury that has been purified by means of ammonia and acetic acid, as above. One c.c. N/10 thiosulphate is equivalent to 0.01423 grm. mercury fulminate, and 1 c.c. N/10 acid to 0.007115 grm. As a rule the fulminate shows the same percentage in both titrations, but in abnormal samples the acidimetric titration sometimes gives a higher result.

A good grey fulminate will show 98 to 99% of the pure substance; white fulminate generally gives results slightly lower, and fulminate purified with ammonia and acetic acid shows 100% within the limits of experimental error.

A blank estimation should be made and corrections applied accordingly. Potassium iodide is liable to contain iodate, which affects the results of the titrations both with acid and iodine. The titration with iodine is but little affected by time, even in the absence of potassium iodide.

Other and cheaper materials can be used instead of potassium iodide to restrain the side reactions, and G. S. Heaven (*J. Soc. Chem. Ind.*, 1918, **37**, 145T.) has recommended the use of boric acid. Of this a quantity equal to that of the fulminate suffices, its action apparently being to neutralise the alkali formed.

In spite of statements to the contrary I have found that in cap compositions containing also antimony sulphide none of the published variations of the thiosulphate method are reliable, but as the result of an investigation of the matter it was found by M. L. Dey in my laboratory that if both potassium iodide and boric acid be added the results are accurate. For 0.3 grm. of fulminate 3 grm. of the iodide and 0.3 grm. of boric acid should be used.

Other methods for the estimation of fulminate mostly depend on the estimation of the mercury. These give the amount of fulminate originally present in the mixture, whereas the thiosulphate method gives the unchanged fulminate. Consequently by carrying out both methods it is possible to estimate the extent to which the explosive has deteriorated. (For the rate of decomposition of fulminate see R. C. Farmer, *Trans. Chem. Soc.*, 1922, **121**, 174; A. Langhans, *Z. ges. Scniess u. Sprengstoffw.*, 1922, **17**, 9, 18 and 26.)

M. Marqueyrol estimates the amount of fulminate in a mixture electrolytically as follows: (*Bull. Soc. Chim.* (iv), **27**, 1920, 448) about 1 grm. is treated with 30 c.c. of a 5% solution of potassium cyanide. This is filtered and the filter is washed with cyanide solution. The liquid is then electrolysed with a current of 4 volts and the mercury is thus deposited as an adherent film which can be washed with water and alcohol and dried over sulphuric acid.

Examination.—A good fulminate, when examined under a low power microscope, is seen to consist of fairly well formed crystals not varying very much in size and almost free from twinned crystals. In brown fulminate the crystals are better formed than in white. The former should contain at least 98% of mercury fulminate as estimated by thiosulphate and titration with acid, and white fulminate not less than 97.5%.

It should be practically free from metallic mercury. This is ascertained by dissolving in strong ammonia and examining the residue under the microscope, or allowing it to act on a piece of gold foil. On treating 0.5 grm. with 100 c.c. of hot water not more than 0.5% should be left undissolved. It should give no reaction for oxalic acid, the test for which may be carried out as follows: dissolve in ammonia, precipitate the mercury with sulphuretted hydrogen, filter, heat the filtrate and add ammonium chloride and calcium chloride. Not more than traces of other impurities should be present.

Supplies of fulminate are sometimes tested for power by exploding a known quantity in a lead block and measuring the expansion of the hole. Or it is made up into detonators and these are tested for brisance in some way, but none of these tests is of much value in judging the quality of the explosive, for if a low result be obtained with a sample that has passed the above chemical tests the fault must lie in the method of carrying out the mechanical test rather than with the fulminate, which is a definite substance. In the British specification, there was formerly a lead block test which was carried out as follows: the block was made of soft lead and was 6 in. high and 4 in. in diameter. It had an axial hole 3 in. long and 1 in. in diameter, and into this 20 grains of dry fulminate were placed and shaken down. This was fired with safety fuse or an electric igniter and the enlargement of the hole was required to be not less than 15 c.c.

SILVER FULMINATE

AgONC Mol. wt. 149.9

This is the only other fulminate that is used commercially, although a number have been prepared in the laboratory. It is much more sensitive than the mercury compound and is only used in minute charges for bonbon snaps and other toy fireworks. In England a thousand of these must not contain more than 15 grains (1 grm.) of the fulminate, and in the work rooms only 1 grain is allowed per person. This substance may be recognised by testing for fulminic acid with phenyl hydrazine, and for silver by the ordinary test.

LEAD AZIDE

PbN_6 Mol. wt. 291.2

Various salts and other derivatives of azoimide or hydrazoic acid, HN_3, have been proposed as substitutes for mercury fulminate, but lead azide is the only one that has been used on a large scale. It is made by precipitating a solution of sodium azide with one of lead acetate or nitrate. It is very important that it be obtained in small crystals, as large ones are very sensitive and may even detonate spontaneously. The liquid should therefore be stirred during the precipitation and the lead solution should be used in excess. A. G. Lowndes recommends that a small quantity of a colloid, such as gelatin or dextrin, be added (*Eng. Pat.*, 1920, **160,953**). The sodium azide can be made by various reactions, but according to H. Kast (*Spreng- und Zundstoffe*, 1921, 429) it is always prepared commercially by the method of R. Stolle (*Germ. Pat.*, 1908, **205,683**) which consists in mixing hydrazine sulphate with the corresponding quantity of aqueous sodium hydroxide solution and shaking with alcohol and amyl nitrite. During the war lead azide was made on a large scale in America and on a considerable one in Germany and France for the detonators of fuses, and it is a constituent of some composite commercial detonators.

Lead azide has a density of 4.8 and can be pressed at much higher pressure than fulminate without rendering it insensitive. 100 c.c. of water dissolve 0.023 grm. at 18° and 0.090 grm. at 70°, but the solubility is increased by the presence of sodium nitrate or acetate. (See Wöhler and Krupko, *Ber.*, 1913, **46,** 2056). 100 c.c. of boiling ether dissolve 0.0027 grm. and 100 c.c. of boiling chloroform 0.0034 grm. (M. Marqueyrol and Loriette, *Mem. Poudres*, 1921, **18,** 94). Acetic acid dissolves it with decomposition. It is insoluble in strong ammonia. Its colour is white, but when exposed to light it is coloured yellow superficially.

Estimation.—If an azide be treated with a solution of iodine and a crystal of sodium thiosulphate be added, nitrogen is evolved according to the equation

$$2NaN_3 + 2I = 3N_2 + 2NaI$$

If the solution contain free mineral acid, sodium acetate must be added (F. Raschig, *Ber.*, **48,** 1915, 2088). Nitrogen is similarly evolved by the action of ceric salts, which are reduced simultaneously to the cerous state.

$$2HN_3 + 2CeO_2 = 3N_2 + H_2O + Ce_2O_3$$

A solution of the azide is put into a flask connected with a nitrometer. Attached to the stopper of the flask is a receptacle containing solid ceric ammonium nitrate or ceric sulphate, 2 to 3 grm. per 0.1 grm. of sodium azide. The flask is immersed for some time in water of the same temperature as the nitrometer, and then tipped up to mix the ceric salt with the solution, which should preferably be neutral. If chlorides be present it must be neutral, otherwise chlorine will be evolved (E. Sommer and H. Pincas, *Ber.*, 1915, **48,** 1965).

The above methods have been devised for the analysis of soluble azides such as that of sodium, and there are no data to show whether they can be adapted for use with an insoluble one such as lead azide. The latter can, however, be estimated by distilling off the hydrazoic acid and estimating it. As it is a comparatively weak acid it can be released by heating even with acetic acid. It can then be distilled into silver nitrate solution and the precipitate of silver azide can be filtered off, washed with water, then with alcohol and ether, dried and weighed (M. Marqueyrol and P. Loriette, *Mem. Poudres*, 1921, **18**, 94). Or the excess of silver nitrate can be titrated.

WOOD-MEAL

This substance which is also called wood-pulp and wood-flour is used not only in the manufacture of nitroglycerin explosives, but also of linoleum, and as an inert absorbent in other industries. The species of wood employed are limited by considerations of colour and weight to the white non-resinous conifers and broad-leafed woods; spruce, white pine and poplar are those most often used. The wood, stripped of bark, is reduced to chips, and then ground in stone mills or in steel burr roller mills, the former being used almost exclusively in Europe, especially in Scandinavia where water-power turbines are employed. The mills are enclosed, and sufficient water or steam is passed in to prevent firing, or air is blown through to keep the mill cool. The fine material is drawn or blown through iron pipes to a screen of bronze wire or bolting cloth. It is then sacked or compressed into bales. The absorptive powers may be improved by boiling with water and drying. In 1900 nearly ten million pounds of wood-meal were used in the manufacture of dynamite in the United States, and in 1909 probably about twenty million pounds.

Wood-meal for the manufacture of explosives should be free from acid and foreign substances, especially particles of metal and grit. The moisture should not exceed 8 or 10%, nor the ash 0.5%. It should absorb nitroglycerin readily. It should not contain chlorides or hypochlorites or other bleaching material which would attack the nitroglycerin and affect the heat test. The heat test of the material mixed with blasting gelatin should be taken. Different factories use meal of different degrees of fineness: it is sometimes required that the whole shall pass through a sieve of 50 meshes to the inch and not more than 30% through a 100-mesh sieve. It should not contain much resin or tannin. The resin may be extracted by ether. Extraction with alcohol will remove also the tannin and some other constituents. Water and dilute acids also remove part of the material. It was found by Snelling and Storm that successive extractions removed the following amounts, calculated on the dry weight, from four samples of wood-pulp:

Extraction with	1	2	3	4	Mean
Ether	2.66	2.78	2.09	1.95	2.37
Cold water	2.57	2.89	2.23	2.84	2.63
Cold hydrochloric acid (1:10)	1.41	0.42	0.53	1.03	0.85
Boiling hydrochloric acid (1:100)	5.91	1.75	3.93	4.83	4.11
Insoluble residue	87.45	92.16	91.22	89.35	90.04

Therefore if wood-meal is estimated by weighing the residue, this should be divided by 0.9 to give approximately the dry weight. If the weight in the air-dry condition be required, a further 10% should be added.

Wood-meal is detected by its appearance under the microscope, and by the coloration it gives with phloroglucinol reagent, which is made by dissolving 1 grm. of phloroglucinol in 15 c.c. of alcohol and 10 c.c. of syrupy phosphoric acid. If a little of the meal be rubbed with 0.5 c.c. of this, it acquires a rose colour changing to carmine. Under the microscope the proportion of grains thus coloured can be roughly estimated.

For the estimation of lignocellulose in wood-meal, see J. F. Briggs, *Analyst*, 1916, **41**, 113.

OTHER COMBUSTIBLES

Although wood-meal is by far the most important, a number of other materials that consist mainly of carbohydrates are used in compounding blasting explosives. Flour of various sorts and starch are used in a number of cases, and in a few potato meal, sago meal, bran, turmeric, quebracho, vegetable ivory, dextrin, sugar and gum. Non-carbohydrates that are occasionally met with are rosin, shellac, albumin, gelatin, soap and various fats and fatty oils, especially castor oil. Hydrocarbons are fairly common constituents: mineral jelly (or vaseline) is present in many smokeless powders and occasionally in blasting explosives. Paraffin wax, naphthalene and liquid hydrocarbons are also used. Charcoal is a constituent of black powder, of course, and in blasting explosives cheaper materials of similar nature such as coal, coke and soot are used occasionally. The German soluble explosive Raschit contains such substances as ammonium nitrocresol sulphonate and the residue obtained from wood cellulose factories.

Many of these substances can be identified under the microscope after separation from other constituents.

There are also a number of inorganic combustibles in use. Black powder contains sulphur, and this also occurs in some American dynamites and other blasting explosives and in fireworks. Antimony sulphide is a constituent of most cap compositions. Blasting explosives of the ammonal type contain aluminium powder coated with paraffin wax to prevent oxidation. As substitutes for aluminium the following have also been used: magnesium, zinc, calcium silicide and ferrosilicon.

GELATINISERS AND STABILISERS

The only volatile gelatinisers, or solvents for nitrocellulose, that are of importance in connection with explosives are acetone and ether-alcohol. Acetone is used to gelatinise the nitrocellulose in smokeless powders containing nitroglycerin and is effective whatever the nitrogen content of the nitrocellulose. In powders not containing nitroglycerin the use of acetone would yield a product which would be too brittle, and consequently for these ether-alcohol is used and it is necessary to make such powders of nitrocellulose of comparatively low nitration which is soluble in ether-alcohol. These volatile solvents are removed from the powder as far as practicable in the drying stoves, and consequently in analysing them there are only slight residual quantities to be estimated. These are dealt with below under the heading "Moisture." In the manufacture of nitrocellulose varnishes other solvents and more complex mixtures are used. Amyl acetate and ethyl acetate are frequently added, and the mixtures often contain an indifferent liquid such as benzine as well as an alcohol such as amyl alcohol and some castor oil and perhaps camphor.

There are also in use a number of gelatinising agents which are non-volatile or nearly so under ordinary conditions. Celluloid, of course, contains a large proportion of camphor which in conjunction with alcohol gelatinises the nitrocellulose which is the other essential constituent. Camphor is also present in some sporting powders, E. C., for instance, and may be recognised in them by the smell, but it suffers from the disadvantage that it is somewhat volatile. Nitro-compounds, such as nitrobenzene and dinitrotoluene, have been used to assist the gelatinisation of smokeless powders, and it has been discovered that they also expedite the gelatinisation of blasting gelatin and other gelatinised nitroglycerin blasting explosives (R. Rintoul, D. Cross and Nobel's Explosives Co., Ltd., Eng. Pat. 14,656 of 1915 and 126,056 of 1916).

Nearly all military smokeless powders contain some substance which is capable of combining with the oxides of nitrogen which are given off in the slow decomposition of nitrocellulose and nitroglycerin, and many sporting powders contain one also. If these oxides are not thus removed they increase the rate of decomposition which may eventually become so rapid that the powder catches fire spontaneously. In cordite the mineral jelly serves this purpose and there is also present a fraction of a per cent. of calcium carbonate which helps to neutralise them. Nitroglycerin blasting explosives also generally contain a small quantity of calcium, magnesium or sodium carbonate and sometimes zinc oxide. Aniline was used at one time for this purpose, and the Italian powder filite contained it, but it has too strong an alkaline reaction and therefore causes decomposition. If, however, a second hydrogen atom attached to the nitrogen be replaced by a phenyl group the resultant compound, diphenylamine, is not too alkaline and is a very satisfactory stabiliser. It has been used as such in Germany for many years and was adopted in France in supercession of amyl alcohol which was found not to have a sufficient stabilising action. It is also present in the American nitrocellulose powder.

Urea has been used largely as a stabiliser for celluloid, but for explosives it is too reactive. Substituted ureas, however, are satisfactory and have the advantage that they are also gelatinisers. In Germany symmetrical diethyl-diphenyl-urea and the corresponding dimethyl-compound have been used under the name of "Centralite," and unsymmetrical diphenyl-urea under that of "Akardite." Sometimes the surface only of the powder is treated with centralite in order to retard the initial rate of burning and render the powder "progressive." It may be stated generally that compounds containing a :CO group are gelatinisers and derivatives of ammonia in which at least two of the H-atoms have been replaced by cyclic radicles are stabilisers. Compounds which contain both groups act in both capacities. Patents have been taken out by W. Rintoul and others dealing with the use of urethanes and other substances of this description both for the manufacture of nitroglycerin blasting explosives (Eng. Pat. 126,056 of 1916, 14,656 of 1915 and 12,743 of 1912) and smokeless powders (Eng. Pat. 166,277 of 1919). This matter is at the present time engaging considerable attention and papers on non-volatile gelatinisers have been published by M. Marqueyrol and D. Florentin (*Mem. Poudres*, 1921, **18**, 150 and 163) J. Desmaroux (*Mem. Poudres*, 1923, **20**, 70) and T. L. Davis (*J. Ind. Eng. Chem.*, 1922, **14**, 1140). It is possible that other substances will come into use; Marqueyrol and Florentin reported specially favorably on dimethylphenyltolylurea and sebacic ether. The latter has the advantage of being comparatively cheap, but probably has little or no stabilising effect.

MINERAL JELLY

This is a sort of crude vaseline or petroleum jelly and consists mostly of semi-solid hydrocarbons, some of which are unsaturated. It is a constituent of cordite and a number of other smokeless powders and is also sometimes added to blasting explosives. The m. p. (dropping point) is now generally determined with Ubbelohde's apparatus and should be between 45° and 55°.

Mineral jelly is readily soluble in ether, petroleum spirit, and various other organic solvents, but is only slightly soluble in alcohol; in a mixture of 4 parts methyl alcohol and 1 part water it is practically insoluble, as also in 70% acetic acid. These last solvents may be used to separate it from nitroglycerin in the ether extract obtained in the analysis of a complex explosive. After distilling off the ether, some 80% methyl-alcohol is added to the residue in the flask, which is then heated on a boiling water-bath. The liquid is allowed to settle for a minute or two, and is then decanted through a small filter or directly into a clean beaker. After repeating this operation about four times the mineral jelly is quite free from nitroglycerin. After the first washing, it is advisable to heat the flask again before adding more alcohol, in order to cause the mineral jelly to adhere to the glass. If any globules of mineral jelly get into the filter or beaker, they must be washed free from nitroglycerin, and then transferred back into the extraction flask, if necessary with the aid of a little ether. After drying in a steam-oven the mineral jelly may be weighed in the extraction flask.

In old cordites the mineral jelly is often partly converted into substances which are soluble in the 80% methyl-alcohol, and consequently the percentage found is low. In such cases the nitroglycerin may be destroyed by heating with an alcoholic solution of sodium hydroxide. The liquid is then neutralised with sulphuric acid, diluted with water and extracted with ether. The extract is evaporated, and the residue dried and weighed.

DIPHENYLAMINE

$(C_6H_5)_2NH$. Mol. wt. 169.2

This is a colourless crystalline substance melting at 53° and boiling at 302°; it is insoluble in water, but readily soluble in alcohol and ether. It is only a feeble base, and its salts are decomposed by water with separation of the amine. Its solution in concentrated sulphuric acid gives with a trace of nitrous acid or other oxidising agents an intense blue coloration.

It may be estimated by saponifying the powder with strong caustic-soda solution, until its structure is destroyed, and then distilling with steam, until the distillate no longer gives a coloration with sulphuric acid containing a little nitric acid. The distillate is then shaken out with ether, and the ethereal solution is dried with calcium chloride and evaporated. The residue is dried over sulphuric acid and weighed. If camphor or other volatile non-basic substance be present, the diphenylamine may be precipitated from the ethereal solution with dry chlorine gas, the precipitate filtered off in a Gooch crucible, washed with ether, dried for thirty minutes at 65° and weighed. Multiplication by the factor 0.83 gives the free diphenylamine (H. Kast, *Spreng- und Zündstoffe*, 1909, p. 958).

Dreger estimates it as tetrabromodiphenylamine (*Z. ges. Schiess u. Sprengstoffw*, 1909, 4, 123). The ethereal solution obtained as above is warmed with alcohol until the ether has been driven off; then bromine is added drop by drop until there is an excess. The liquid is diluted with twice its volume of water and boiled until the alcohol and bromine have been driven off and the volume has been reduced to half. The precipitate of tetrabrom-diph-enylamine is filtered off, washed with warm water and dried at 98° to 100° until the weight is constant. Multiplication by the factor 0.3487 gives the weight of diphenylamine.

In France diphenylamine, together with nitroso-diphenylamine, is estimated in Poudre B as follows: (A. Buisson, *Problème des Poudres*, 1913, p. 127). The powder is cut into small pieces and 10 grms. are placed in a Jena glass flask of 1 litre capacity, together with 500 c.c. of a 6% solution of caustic soda. The flask is connected through a condenser with another flask on which is a mark showing 300 c.c. The contents of the litre flask are boiled. The powder is destroyed by the soda, and the nitroso-diphenylamine is converted into diphenylamine, which passes over with the steam together with the rest of the diphenylamine. When 300 c.c. of distillate have been collected, the condenser is washed out with 50 c.c. of chloroform, which is added to the contents of the receiver. To this are also added 2 c.c. of 10% hydrochloric acid, and by means of a burette 40 c.c. of bromine water. The flask is shaken vigorously every five minutes for half an hour, by which time the bromination is complete, and the chloroform layer has dissolved the product and the excess of bromine, except a small portion, which colours the water a pale yellow. About 10 c.c. of 20% solution of potassium iodide are then added, and the liquid is titrated with N/10 thiosulphate, some starch solution being added before the end. The nitro-derivatives of diphenylamine are attacked somewhat by the soda, but they give no diphenylamine. One molecule of diphenylamine causes the disappearance of 8 atoms of bromine:

$$(C_6H_5)_2NH + 8\,Br = (C_6H_3Br_2)_2NH + 4\,HBr$$

Diphenylamine for the manufacture of Poudre B must be either in the form of small crystals, white or slightly yellow, or in fused crystalline lumps of uniform colour, slightly yellow. It must not contain chloride or carbonate of ammonium or sodium, as their presence would indicate that the substance had been badly purified. Its m. p. must be between 52° and 53°. It must not contain more than 0.001% of aniline or toluidine, as these primary amines attack nitro-cellulose (Buisson, *loc. cit.*, p. 43). These are detected by adding the powdered diphenylamine to a solution of bleaching powder.

If an explosive contain diphenylamine it will on storage become blue, and the colour will gradually darken until it becomes practically black. This discoloration is not to be taken as an indication that the life of the powder is drawing to a close, for it appears comparatively early. The gradual exhaustion of the stabiliser can, however, be followed readily by extracting it from the powder and applying certain reactions. (See A. Buisson, *loc. cit.*, p. 126.) The decomposition of the nitro-cellulose and the consequent liberation of oxides of nitrogen converts the diphenylamine first into diphenyl-nitrosamine, then into nitro-diphenyl-nitrosamine, dinitro-diphenylamine and finally trinitro-diphenylamine (See also P. Juillard, *Bull. Soc. Chim.*, 1905, **33**, 1172.) The nitration of the stabiliser does not proceed beyond the trinitro-derivative, and the presence of this compound indicates that the life of the powder is nearing its close.

$(C_6H_5)_2NH$	$(C_6H_5)_2N.NO$	$C_6H_4(NO_2).N(NO).C_6H_5$
diphenylamine	diphenyl-nitrosamine	nitro-diphenyl-nitrosamine
$(C_6H_4NO_2)_2NH$	$C_6H_4(NO_2).NH.C_6H_3(NO_2)_2$	
dinitro-diphenylamine	trinitro-diphenylamine	

To test for these different compounds 10 grms. of finely divided powder are digested for twenty-four hours with 100 c.c. of alcohol. For diphenyl-nitrosamine 5 c.c. of the solution are boiled with 1 c.c. of a 5% solution of α-naphthylamine: the nitrosamine gives a fine red colour. The quantity of it present can be estimated approximately by comparing the colour with that given by known quantities of nitrosamine, but in this case the powder must be extracted for several days with successive quantities of alcohol, and a larger quantity of solution must be taken.

The dinitro-diphenylamines are detected by adding a few drops of alcoholic potash or soda to 5 c.c. of the alcoholic extract. They give a red coloration, as also do the trinitro-diphenylamines. But the latter can be distinguished by the red coloration they give when a few drops of a saturated alcoholic solution of potassium cyanide are added to 5 c.c. of the alcoholic extract.

The quantity of unchanged diphenylamine, together with the diphenyl-nitrosamine, estimated as described above, gives a measure of the amount of stabiliser still available in the explosive, for the nitrosamine is an efficient stabiliser also. The quantity of nitrosamine is at a maximum when from a half to two-thirds of the life of the powder has elapsed. (E. Berger, *Bull. Soc. Chim.* (IV), 1912, **11**, 1.)

OTHER STABILISERS AND GELATINISERS

No analytical methods have been published for the other substances that are used or have been proposed. The substituted ureas mentioned above are all readily soluble in alcohol.

Centralite 1, symmetrical diethyldiphenylurea, $(C_2H_5)(C_6H_5)$:-N.CO.N:$(C_2H_5)(C_6H_5)$, is made by the action of ethyl aniline on phosgene and melts at 72°.

Centralite 2, symmetrical dimethyldiphenylurea, is similarly made from methyl aniline and phosgene, and has a m. p. of 118°. (M. Marqueyrol and D. Florentin, *Mem. Poudres*, 1921, **18**, 150.)

Akardit, unsymmetrical diphenylurea, $H_2N.CO.N:(C_6H_5)_2$, melts at 189°, and crystallises in long colourless crystals. When warmed gently with sulphuric acid containing a little nitrous acid it gives a blue solution. On heating with alcoholic potash it is decomposed into diphenylamine, ammonia and carbon dioxide.

Dimethylphenyl-*o*-tolylurea, $(CH_3)(C_6H_5)$:N.CO.N:$(CH_3)(C_6H_4.\text{-}CH_3)$, is a viscous liquid which could not be made to crystallise. It mixes in all proportions with alcohol and ether, but is insoluble in water.

Symmetrical dimethyldi-*o*-tolylurea melts at 89° and boils at 193–5° under a pressure of 13 mm. 100 grm. alcohol dissolve 72 grm. at 20°.

Sebacic ether, $C_2H_5.O.CO.(CH_2)_8.CO.O.C_2H_5$, is a mobile liquid freezing at 4–5° and boiling at 307–8° at atmospheric pressure. It has a density of 0.968 at 15°.

MOISTURE (VOLATILE MATTER)

All explosives that have been gelatinised wholly or partly with a volatile solvent retain more or less of it. In the case of the larger sizes of Cordite M. D. this amounts frequently to more than 1% and nitro-cellulose powders, in which there is no nitroglycerin, generally contain several per cent., which it is impracticable to drive off in the drying stoves, as it is retained by the colloid with great obstinacy.

In the case of explosives not containing nitroglycerin, camphor, or any other constituent that is slightly volatile, the material is ground and sifted, and 2 grm. are weighed out on to a watch-glass and dried in an oven at a suitable temperature to constant weight. As a rule, it is not advisable to take for this purpose material that has been ground more finely than is laid down in the directions for the heat test, because the very fine material loses some of its volatile matter during grinding, sifting and weighing. The temperature of the oven is usually somewhere between 65° and 100°. Explosives that are thoroughly stable will withstand the latter temperature for several hours without undergoing a sufficient amount of decomposition to affect the results. In the case of unstable materials a lower temperature must be employed, however, and in extreme cases the drying should be carried out at the ordinary temperature in a vacuum desiccator.

American Method.—In order to avoid losses during grinding and weighing, in the United States the nitro-cellulose powder is merely cut up and is degelatinised by dissolving in ether-alcohol and reprecipitating with water (E. M. Weaver, *Military Explosives*, 4th Ed. (1912), 202). Slices are cut from at least 5 average grains in the case of large-calibre powders; with smaller powders whole grains may be taken or slices may be cut from a number. The sample thus obtained is thoroughly mixed and 1 grm. is weighed out. This is dissolved in 150 c.c. of ether-alcohol (2:1), and when solution is complete the nitro-cellulose is precipitated by the gradual addition of a suitable amount of water, and the mixture is evaporated on a steam-bath. When evaporation is apparently complete, it is dried for one hour at 95° to 100°, or in a vacuum drier at 50° and weighed. The loss of weight, corrected for the residue in the solvent and water used, is called the "total volatiles, as packed."

"Moisture" is also estimated. This is estimated by drying at least 5 grains, weighing not less than 20 grm., for two hours in a vacuum drier at 50° to 60°. The difference between the "total volatiles" and the "moisture" is called the "residual solvent." In the American small-arms powder the "total volatiles" must not exceed 3.15%.

French Method.—In France a similar precipitation method is used for estimating the volatile matter is Poudre B. (A. Buisson, *Z. ges. Schiess u. Sprengstoffw.*, 1913, **8**, 288.) But if it contain diphenylamine, which is slight volatile, the estimation is made by drying *in vacuo* at the ordinary temperature.

Estimation of Water.—For the estimation of the water only, in substances which also contain acetone and other volatile compounds. A. Dupré recommended the use of calcium carbide (*Analyst*, 1906, **31**, 213). The ground material is put into a tube 1 cm. wide and 10 cm. long and covered first with a layer of dry sand and then with a layer of carbide 5 cm. high. The tube is connected with a nitrometer filled with saturated brine, and heated in a water-bath to 100°. The moisture reacts with the calcium carbide, producing acetylene. The volume of gas evolved is slightly less than that calculated, when known volumes of water are present; it varies somewhat with different samples of carbide. The coefficient of the carbide may be determined by an experiment with a known weight of pure ammonium oxalate, which contains 12.67% of water of crystallisation. The carbide used by A. Dupré gave 1 c.c. for 0.001725 grm. water (See also Huntly and Coste, *J. Soc. Chem. Ind.*, 1913, **32**, 63; and Campbell, ibid., p. 67). If the smokeless powder be exposed to the air, the amount of water in it varies with the hygrometric state of the atmosphere, and therefore with the season of the year (See Hansen, *Z. ges. Schiess u. Sprengstoffw.*, 1911, **6**, 401).

Moisture in Nitroglycerin Explosives.—In estimating the moisture in nitroglycerin explosives difficulty arises from the fact that nitroglycerin itself is slightly volatile. But investigations carried out at the Royal Gunpowder Factory, Waltham Albey, by L. W. Dupré and A. Marshall, showed that the difficulty could be overcome by the use of a special apparatus, consisting of an aluminium dish covered with a glass cone, so as to leave only a very slight space between them for the escape of the vapour of water and organic solvent (See A. Marshall, *J. Soc. Chem. Ind.*, 1904, **23**, 154).

The apparatus is warmed and allowed to stand for half an hour in a desiccator to acquire constant weight. Then 5 grm. of the sample are placed in the aluminium dish, the glass cone is put over it, and the whole is weighed. The apparatus is then stood upon a metal plate heated below by boiling water or steam: the top of an ordinary boiling-water oven is suitable. Here it is allowed to stand until the weight is practically constant. In the case of cordite, Mark I, or ballistite, or blasting gelatin, an hour is sufficient; Cordite M.

D. requires two hours. The apparatus is then removed to the desiccator, allowed to stand for half an hour and weighed. The loss of weight is the amount of moisture (volatile matter) in the explosive taken. Any nitroglycerin that is driven off from the powder by the heat is condensed on the glass cone. The loss of nitroglycerin from the apparatus is less than 0.01% and the results are very consistent. The material should be ground and sifted in the same manner as is laid down in the instructions for the heat test.

The same method can be used for explosives containing diphenylamine or nitro-toluenes. Mono-nitro-toluene is not very much more volatile than nitroglycerin, and consequently there will be but little loss. Dinitro-toluene is less volatile than nitroglycerin, and trinitrotoluene, if free from mono- or di-nitro-toluene, or other volatile impurity, loses no appreciable weight even when dried on open watch-glasses. The moisture cannot be estimated in celluloid by this method, as camphor is more volatile.

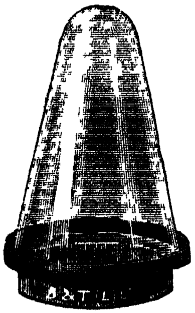


FIG 27.—Apparatus for the determination of moisture in nitroglycerin explosives. (From Marshall's Explosives.)

The U. S. Bureau of Mines estimates the moisture in dynamites by placing 2 grms. of the explosive on a 3-in. watch-glass in a desiccator containing strong sulphuric acid at about 20°, and weighing after three days. An approximate estimation may be made by desiccating in this way for twenty-four hours and multiplying the loss in weight by the factor 1.111. Or the loss of weight in a vacuum desiccator in twenty-four hours may be taken without correction as the approximate amount of moisture (*Bureau of Mines Bull.*, No. 51, 29).

ANALYSIS OF COMPLEX EXPLOSIVES

Both for qualitative and quantitative analysis it is generally best to make a preliminary separation of the constituents of the explosive by extracting it with various solvents. The first extraction is with ether which dissolves out nitroglycerin and similar substances, nitro-aromatic compounds, sulphur, fats and oils, naphthalene and resins. Pure ether should be used, not methylated, as it extracts less from wood-meal or nitrocellulose, if present. If the explosive contain much moisture it should first be dried partially by standing in a desiccator over sulphuric acid for 24 hours. The extraction can generally be carried out in a beaker in which the sample is treated with successive portions of the solvent, but gelatinised smokeless powders should be ground finely, soaked over night in ether and extracted in a Soxhlet next day. For the methods of estimating the nitroglycerin and nitro-compounds see above. Nitroglycerin can be separated from sulphur, mineral jelly and various other substances by extracting with 80% methyl alcohol or 70% acetic acid (see above under "Mineral Jelly"). Resin can be estimated by saponifying with alcoholic potash, diluting with water, extracting with ether, and acidifying the aqueous liquid. The resin is thus precipitated and can be estimated by extracting with ether, evaporating down and weighing or by again saponifying with a known quantity of alkali and titrating back the excess.

The residue from the ether extraction is next extracted with water. If the explosive contain flour or starch the water should be cold, as hot water would gelatinise it. Cold water should also be used for samples containing wood-meal, as this gives up some more matter to hot water. The water extract contains the inorganic nitrates, chlorates, perchlorates and chlorides, ammonium oxalate and any other soluble salts, also glycerin and aniline hydrochloride, if present, and part of the dextrin, gum, starch and gelatine, the amount depending on the coagulating power of the salts. In the presence of starch Snelling and Storm recommend the use of a porous alundum filter for filtering off the aqueous extract. Gum arabic, which is sometimes added as a binding agent, may be detected by adding basic lead acetate, with which it gives a precipitate. In some cases chemical analysis fails to distinguish between two or more mixtures of salts having the same ultimate composition. It is, for instance, impossible from results of chemical analysis to distinguish a mixture of ammonium nitrate and sodium chloride in equivalent proportions from one of sodium nitrate and ammonium chloride. In such cases C. G. Storm and A. L. Hyde separate the salts by the use of a liquid in which one or more of the salts floats whilst others sink (*Bureau of Mines Technical Paper* 78; Also A. Marshall, Explosives, 2nd ed., 1917, p. 677). Mixtures of bromoform (sp. gr. 2.83) and chloroform (sp. gr. 1.49) are suitable for the purpose.

The residue insoluble in water may contain nitrocellulose, calcium carbonate, magnesium carbonate, kieselguhr, wood-meal, flour, etc., charcoal, graphite, aluminium or other metal and calcium silicide. Treatment with dilute hydrochloric acid will dissolve the carbonates and the starchy materials, as also the metals. By examination under the microscope the remaining substance or substances may be identified. Dextrin, gums and gelatin are generally estimated by difference, but they give qualitative reactions by which they can be identified in most cases. Starch may be recognised by the fact that it dissolves in boiling water and is coloured blue by iodine. Nitrostarch is not coloured by iodine. Wood-meal gives a characteristic colour with phloroglucinol reagent. Calcium silicide may be recognised by the fact that it dissolves in dilute hydrochloric acid, giving off hydrogen and silicon hydride, which is spontaneously inflammable.

An enormous number of different substances have been proposed at one time or another as constituents of explosives, but in this article only the important ones are dealt with. For a complete list of the constituents of explosives in actual use see the index of Marshall's "Dictionary of Explosives" (Published by Churchill, 1920). For micro-photos of some of the materials that may be present see C. G. Storm, Analysis of Permissible Explosives, 1916, U. S. *Bureau of Mines Bull.* 96. For other general literature of the subject see Bibliography at the end of this article

Smokeless powders for rifled firearms at the present time always consist largely of gelatinised nitrocellulose. Many of them also contain nitroglycerin and there is generally a stabiliser. Non-volatile gelatinising agents should also be looked for. Soluble salts are seldom present, although proposals have been made to incorporate such substances as potassium chloride and potassium bioxalate with powders in order to eliminate the muzzle flame. It is, however, more usual to add such substances as a separate charge in the gun. They have the disadvantage that they increase the smoke and the residue in the gun. These powders require to be reduced to very fine state of division for analysis.

Smokeless powders for shot-guns also always contain a large proportion of nitrocellulose. Except Sporting Ballistite they do not contain nitroglycerin. Bulk powders are often only partially gelatinised and generally contain oxidising salts. The most usual composition is a nitrocellulose only partially soluble in ether-alcohol, mixed with potassium and barium nitrates and a nitro-compound to assist the gelatinisation.

Smokeless powders should always be examined as to their stability. A determination of the solubility of the nitrocellulose in ether-alcohol should be carried out, as also an estimation of its nitrogen. If a volatile solvent has been used to gelatinise it, its nature can generally be deduced from the smell when the powder has been heated in a closed test tube, as in the heat test.

Military high explosives for filling shells always contain aromatic nitro-compounds and often consist entirely of them. Before the war the British high explosive was lyddite, which is picric acid that has been melted and poured into the shell. During the war it was superseded largely by amatol which is a mixture of ammonium nitrate and trinitrotoluene. Amatol $^{80}/_{20}$ contains about 80% ammonium nitrate and 20% trotyl and was the mixture used most largely; it cannot be poured, but was either pressed, into the shell by hydraulic presses or stemmed in after being made soft by heat. It is doubtful whether amatol will continue to be used in peace time on account of the deliquescent nature of ammonium nitrate.

In Germany trotyl was generally used before the war under the name of Füllpulver, but during the war it was necessary to mix ammonium nitrate with it, as in England, in order to make the supplies suffice. The mixture was called "Gestrecktes Füllpulver" and the most used composition was about 40% ammonium nitrate, for which the abbreviated term was Fp. 60/40. Many other nitro-compounds were also used in Germany, and their air bombs and torpedo war heads often contained such mixtures as trotyl and hexanitrodiphenylamine on account of their great brisance.

The French used ammonium nitrate mixtures comparatively little. A large number of different mixtures of nitro-compounds were employed, but most of them contained picric acid or a similar compound.

For military demolitions the English still use compressed wet gun-cotton fired by a primer of dry gun-cotton, but other nations generally have compressed blocks of trotyl. For such purposes as road building and charging military mines military engineers generally use the ordinary commercial explosives such as gelatin dynamite.

Methods for the identification of these various nitro-compounds have already been given. Estimations of the nitrogen and setting point are of importance, and it is often desirable to ascertain the apparent density.

Blasting explosives are liable to contain a greater variety of ingredients. Of the explosives containing a large proportion of nitroglycerin the oldest is dynamite No. 1 which consists of this substance absorbed in 1/3 its weight of kieselguhr and usually coloured with iron oxide, but this is little used now. The dynamites now made have the nitroglycerin absorbed in an "active base," consisting generally of wood-meal and potassium or sodium nitrate. In England the nitroglycerin is always gelatinised by means of a small percentage of collodion cotton, and generally a non-volatile agent is added to assist the gelatinisation. A small quantity of calcium or magnesium carbonate is also introduced as a stabiliser. Gelignite is also an explosive of this class. In American dynamites the nitroglycerin is not as a rule gelatinised and part of the wood-meal is often replaced by flour and sulphur. In ammonia dynamites a considerable proportion of the nitroglycerin is replaced by ammonium nitrate, and in "Red Cross" and other American low-freezing dynamite by nitrotoluene or other nitro-compounds. One of the advantages of nitroglycerin explosives is that they are plastic, but at least 20% of nitroglycerin, whether gelatinised or not, is required to produce this effect. These explosives should be tested to ascertain that they are not liable to exude. The gelatinised explosives are also liable to become dangerously insensitive, and it is often desirable to test them for this as well. The simplest and the most powerful of these explosives in blasting gelatin which consists simply of nitroglycerin gelatinised with about 7% of collodion cotton.

Liquid oxygen explosives are now used in Germany on a large scale for mining. They are made by soaking a cartridge of porous combustible material in liquid oxygen and firing promptly before too much of the oxygen has evaporated away. Soot made from naphthalene and contained in a cotton bag is the combustible most used. Naphthalene is sometimes mixed with the soot. Kieselguhr impregnated with mineral oil has been recommended in America The great disadvantage of these explosives is, of course, that they must be fired without loss of time.

Ammonium nitrate explosives are used more and more on account of their low cost of production and safety in handling. Their principal disadvantage is that they are decidedly hygroscopic, and the cartridges must therefore be well coated with paraffin wax. In order to render them reasonably sensitive to detonation they always contain either a small proportion of nitroglycerin or a di- or trinitro-aromatic compound. In Germany, however, during the war some explosives were made by mixing ammonium nitrate with sodium acetate or dicyandiamide.

Ammonal contains, in addition to ammonium nitrate and trinitrotoluene, aluminium powder and a little charcoal, and there are several other similar explosives containing either aluminium or magnesium or calcium silicide. The metallic powders are coated with paraffin wax to prevent corrosion.

Potassium chlorate explosives always contain some soft ingredient, such as castor oil or paraffin wax, to diminish the sensitiveness. Even then they are less safe in handling than other types of explosives. Cheddite, which is the most largely used of these compositions, usually contains about 5% of castor oil and some dinitrotoluene and nitronaphthalene. In Steelite and the German explosive Silesia oxidised resin is used instead of castor oil. "Sprengel" explosives, which are made by mixing a liquid with a solid porous body just before use, generally have potassium chlorate as the latter ingredient, and kerosine or nitrobenzene or a mixture of them for the former, but they are not much used now on account of the difficulty of attaining uniform results. In Germany during the war a number of what may be considered ready-mixed Sprengel explosives were introduced on account of the scarcity of nitrogen compounds, but the only one that is used much now is Miedziankit, which contains 90% chlorate and 10% kerosene. Chlorate mixtures never contain ammonium salts, as ammonium chlorate, which would be formed, is liable to explode spontaneously. Sodium chlorate is not much used, as it is almost as expensive as the potassium salt and is hygroscopic.

Potassium perchlorate, unlike the chlorate, is a perfectly stable compound, and the explosives made with it are much less sensitive. It is even less hygroscopic than the chlorate and consequently is a very satisfactory oxygen carrier; its only disadvantage is its comparatively high price. It is sometimes added to coal mine explosives, because the potassium chloride formed on explosion helps to damp the flame. In ammonium nitrate explosives it diminishes the the insensitiveness to detonation.

Ammonium perchlorate is also used to some extent as an oxidising ingredient in spite of its cost. It is usually mixed with di- or trinitrotoluene and paraffin wax or castor oil. Unless the explosive contain an equivalent quantity of sodium nitrate or similar substance hydrogen chloride is generated on explosion, and this is very dangerous to miners.

Coal mine explosives are specially composed so as not to be liable to ignite fire-damp or coal dust. They may belong to any of the types that have just been mentioned with the addition of some substance to cool the flame. The substances most used for this purpose are the chlorides of ammonium, sodium and potassium and ammonium oxalate. Ammonium sulphate may be met with and hydrated salts such as sulphate of sodium or magnesium. The last named and alum are components of some American explosives of this class, as also aluminium sulphate and gypsum. The compositions of British "permitted explosives" are given in the "Explosives in Coal Mines Orders" issued from time to time by H. M. Inspectors of Explosives. Ammonium nitrate explosives are those most used for this purpose at the present time.

Fireworks contain mixtures which are more or less explosive. Rocket composition is the same qualitatively as black powder, that is a mixture of saltpetre, charcoal and sulphur, but the proportions are different and they are not incorporated so intimately. Many of the ingredients of firework mixtures are inorganic. A. S. H. Brock give the following list of the principal ingredients used in pyrotechny at the present time ("Pyrotechnics," 1922, p. 181)

FORCE AND SPARKS COMPOSITIONS

Saltpetre
Sulphur
Charcoal
Mealed gunpowder
Iron borings
Steel filings
Zinc filings
Aluminium and alloys
Magnesium and alloys
Lampblack
Orpiment (sulphide of arsenic)
Black antimony (sulphide of antimony)

CHLORATE COLOUR COMPOSITIONS

Chlorate of potash or perchlorate of potash.

Red	Nitrate of strontia Carbonate of strontia Sulphate of strontia	Blue	Carbonate of copper Sulphide of copper Arsenite of copper Calomel
Green	Nitrate of baryta Chlorate of baryta Carbonate of baryta	Yellow	Oxalate of soda Carbonate of soda

For extra brightness magnesium added.
Secondary tints obtained by mixtures of the above.

NON-CHLORATE COLOUR COMPOSITIONS

Saltpetre
Sulphur
Charcoal
Black antimony
White arsenic
Orpiment
Aluminium
Magnesium
Sulphate of copper
Borax

BURNABLES	AGGLUTINANTS	SOUND PRODUCING
Shellac	Shellac and spirit	Gunpowder
Pitch	Starch paste	Guncotton
Stearine	Gum water	Picrate of potash
Paraffin	Linseed oil	Chlorate of potash
Sugar of milk	Dextrine	Aluminium
Linseed oil		

Mixtures of chlorates with sulphur or a sulphide are much liked by makers of fireworks because they are easy to ignite and burn well, but they are liable to be dangerously sensitive and may under some conditions ignite spontaneously. They are consequently not allowed in England and some other countries for the manufacture of fireworks.

DETONATOR AND CAP COMPOSITIONS

The function of a detonator is, when excited by a blow or flame, to detonate and thus cause the detonation of a charge of explosive. That of a cap is, when similarly excited, to generate a flame which starts the burning of a charge of gunpowder or propellant. Until recently the main charge of a detonator always consisted of fulminate of mercury either alone or mixed with a small proportion of potassium chlorate, but now they are often more complex. As fulminate is not a powerful explosive it is advantageous to replace a large proportion of it by a nitro-compound such as tetryl or trotyl. This is pressed into the copper capsule first, then about 0.3 grm. of fulminate is introduced and pressed down, and finally a "reinforcing cap" is introduced and pressed down in its turn. The latter is a copper or brass thimble with a small hole in the base and serves to retain the fulminate in position and confines the detonation. As these composite detonators are cheaper than those containing only fulminate mixture, as well as more effective, they are coming rapidly into use.

Fulminate is not only expensive, but also has the disadvantage that it is rendered insensitive by the absorption of moisture or by excessive pressing and decomposes on prolonged storage at a high temperature. Many attempts have therefore been made to find a satisfactory substitute, but the only such substance that has hitherto achieved practical success is lead azide. This has the disadvantage that it reacts with copper to form highly sensitive copper azide. The capsules are therefore sometimes made of aluminium. Composite detonators containing a nitro-compound and azide are also made.

An electric detonator is a combination of an ordinary detonator with an electric fuse. The latter consists of a small piece of wire of platinum alloy, about 0.03 mm. in diameter, soldered to the ends of two copper leading wires and sourrounded by a small quantity of some composition which is easily ignited. This is generally a tuft of gun-cotton, either alone or mixed with mealed powder, or with potassium chlorate and antimony sulphide. This fuse is inserted into the detonator and sealed in with sulphur or asphaltum or both. When a current is passed through the wires the platinum bridge becomes incandescent and ignites the ignition charge, which causes the detonator to explode.

The extraction of the charge from a detonator is an operation which requires to be carried out with due precautions, as it is necessarily decidedly sensitive and is quite sufficient to blow off several fingers. An appliance should therefore be erected whereby the fuse can be pulled out by operating a lever on the other side of a steel screen, and then the shell of the detonator should be cut by pressing in a similar manner a triangular cutter into the mouth of the capsule. The metal can then be torn apart by pulling it from a distance. For ordinary non-electric detonators C. A. Taylor and W. H. Rinkenbach recommend rolling them carefully between two pieces of smooth hard-wood board and dump out the loosened charge after each rolling (Analysis of Detonating and Priming Mixtures, U. S. Bureau of Mines Technical Paper 282, 1922, p. 12).

Percussion caps contain such a small quantity of explosive in each that no great precautions are necessary in removing the charges. The composition can be loosened by squeezing the cap with a pair of pliers and then removed with a sharpened piece of wood. The most common mixtures contain mercury fulminate, antimony sulphide, Sb_2S_3, and potassium chlorate, to which may be added sulphur, mealed gunpowder or glass to render it more sensitive. The fulminate is sometimes omitted, but then the composition is less sensitive. The antimony sulphide has sometimes been replaced by other inorganic combustibles, such as lead thiocyanate or ferrocyanide, but apparently these mixtures have not been very successful, probably because, unlike antimony sulphide, these substitutes do not possess the right degree of "grittiness." Gelatin is sometimes used in compounding the mixture, and the surface is generally covered with shellac varnish or lead foil or both.

It will be seen that these compositions are not as a rule very complex, and the principal difficulties are caused by the smallness of the quantities available. For the analysis of an unknown mixture it is best to make a separation by the use of successive solvents, and the following scheme for a qualitative analysis combined with a rough quantitative one has been given by M. Marqueyrol and P. Loriette (*Mem. Poudres*, 1921, **18**, 93). The composition is first extracted with ether, which dissolves out the nitro-compounds and sulphur. The extract is evaporated and weighed, and the nitro-compounds are identified by the methods already given. The residue is then treated with a few c.c. of cold water, which removes such substances as chlorates and nitrates. It is next extracted with a 5% solution of potassium cyanide, which dissolves the fulminate, which may be estimated by electrolysis with a current of 8 volts and weighing the deposit of mercury. Or a qualitative test for fulminate may be made by neutralising with nitric acid, which causes it to be precipitated in fine white crystals.

The material insoluble in the cyanide is put into a small distilling flask with a few c.c. of water, acidified with 1 c.c. of acetic acid, and distilled into a solution of silver nitrate. If lead azide be present, there will be formed a precipitate of silver azide, which is filtered. washed with a little water, then with alcohol and ether, dried and weighed. From the weight the amount of lead azide can be calculated approximately. The silver azide can be identified by the way it behaves on being struck or heated. This method can also be applied before the treatment with potassium cyanide.

The residue from the above will contain antimony sulphide and glass powder, if present, and they can be identified under the microscope or by chemical tests. Fulminate can also be estimated by the thiosulphate method, and the antimony sulphide can be estimated in the insoluble residue by titration with iodine by the method given by H. Brownsdon (*J. Soc. Chem. Ind.*, 1905, **24**, 381).

STABILITY

That the nitric esters of cellulose and glycerin decompose spontaneously at all temperatures, but much faster at high ones, has long been recognised, having first been demonstrated by W. Will in 1900. Work carried out in England during the war has proved that all explosives evolve gas more or less in accordance with the equation $V = k^t \times c$, where V is the velocity of the decomposition, t is the temperature and k and c are constants. For a difference of 5° C. the rate of decomposition is about doubled as a rule. A table given by Sir R. Robertson makes it possible to compare directly the stability of a considerable number of very different substances (*Trans. Chem. Soc.*, 1921, **119**, 13).

	Gas evolution at 140°	Temp. coeff. for 5°	
m-Dinitrobenzene	0		Not measurable at 140°
2: 4-Dinitroaniline	0		Not measurable at 140°
1:3:5-Trinitrobenzene	0		0.05 at 180°
2:4:6-Trinitromesitylene	0.003		8.4 at 180°
Lead azide			40 at 180°
2:4:6-Trinitro-*m*-xylene	0.5		8.0 at 160°
2:4:6-Trinitrophenol (picric acid)	0.6	2.3	
2:4:6-Trinitroaniline	4		
1:2:4-Trinitrobenzene	8		
2:4:6-Trinitrotoluene (trotyl)	9	1.85	
2:4:6-Trinitro-*m*-cresol	10		
2:3:4-Trinitrotoluene	13		
2:3:5-Trinitrotoluene	(24)		1.5 at 120°
2:4:5-Trinitrotoluene	32	1.8	
2:4:6-Trinitroanisole	32		
2:4:6-Trinitrophenylmethylnitroamine (tetryl)	(128)	1.95	8 at 120°
2:3:4: 6-Tetranitroaniline	(288)		18 at 120°
3:4:5-Trinitrotoluene	(352)		22 at 120°
2:4:6-Trinitro-3-hydroxyphenylmethylnitroamine	(370)		23 at 120°
Mercury fulminate	(1,500)	1.7	2.5 at 80°
Cellulose nitrate (guncotton, N 13 %)	(5,000)	1.9	2,500 at 135°
Glyceryl trinitrate (nitroglycerin)	(86,000)	2.2	1,660 at 115°

The figures in brackets were estimated by extrapolation. The gas evolution is in c.c. per kilo. per hour after heating for 40 hours to render the rate uniform.

These rates of decomposition depend largely on the conditions and especially on the presence or absence of traces of various impurities that act as catalysts, but it will be seen that the nitric esters of cellulose and glycerol are considerably more unstable than any of the other explosives that are used on a large scale. In the case of fulminate there is a curious quiescent period of considerable duration before active decomposition sets in (R. C. Farmer, *Trans. Chem. Soc.*, 1922, **121**, 174; A. Langhans, *Z. ges. Schiess u Sprengstoffw.*, 1922, **17**, 1) but this matter requires further investigation. The nitric esters on decomposition form acid substances which acts as catalyts, and consequently the rate of decomposition may eventually become so rapid that the explosive catches fire and burns violently or explodes, especially if stored in a hot place. This is a danger which always has to be borne in mind in the case of propellants and nitroglycerin blasting explosives, which consequently have to be tested periodically to ascertain their stability A considerable number of different tests have been devised from time to time to ascertain the rate at which these explosives are decomposing, but unfortunately they are all more or less unsatisfactory, because the rate, even in the case of a fairly unstable powder, is very slow unless the temperature be raised considerably above 100°, and this introduces a new set of conditions. The majority of the stability tests may be divided into 4 classes: (1) the trace tests, in which the explosive is heated at a moderate temperature, and traces of oxides of nitrogen are tested for; (2) the fume tests, in which it is heated at a high temperature until red fumes appear or other considerable change takes place; (3) keeping tests, in which it is kept at a moderate temperature for months, or even years, until decomposition has proceeded so far as to be recognisable; and (4) chemical tests in which products of decomposition are detected or estimated by analytical methods.

All these classes of tests except the last are affected more or less by the amount of moisture in the explosive. In some of the methods described below account has been taken of this factor, but it is an aspect of the question which requires much more investigation.

(1) TRACE TESTS

The most important of these is the ordinary "heat test," often called the Abel test after Sir Frederick Abel, although its introduction was largely due to the work of the late Dr. A. Duprè.

ABEL HEAT TEST

The British Home Office rules for carrying this out were published in the "Memorandum on the Heat Test as applied to Explosives" (H. M. Stationery Office, 2nd Feb., 1914, price 1s. 6d.), and also in the "First Report of the Departmental Committee on the Heat Test of the same date. They are as follows:

I. Apparatus and Materials Employed

TABLE I

Specification or Figure	Article	
A	Acid, acetic, 2 oz. bottle	1
	Balance	1
Fig. 10	Bath, water Bath, water, for hot water heating[1]	1
	Beaker, glass, ½ litres	1
	Bottle, dropping, brown glass, 1 oz. (for glycerine and water mixture)	1
	Bottle, glass-stoppered, brown glass, 1 oz. (for standard tint papers)	1
	Bottle, glass-stoppered, brown glass, 2 oz. (for test papers)	1
	Brush, cleaning	2
	Brush, cleaning, test tube	1
Fig. 10	Burner, gas, Argand, and screen	1
Fig. 9	Caps, for test tubes	A supply
B	Chalk, French	A supply
	Forceps, lifting, heat test papers	1
	Funnel, aluminium	1
	Funnel, glass	1
C	Glycerin, 1 oz. bottle	1
	Knife, cordite	1
Fig. 10	Lid, water bath	1
Fig. 9	Mill, cordite	1
	Needle, piercing, heat test papers	1
	Oven, water	1
D	Paper, filter	A supply
D	Papers, filter, 5.5 cm	A supply
	Papers, standard tint	A supply
E	Papers, test	A supply
	Pestle and mortar, wedgwood ware	1
	Plate, glass, resting heat test papers on when piercing.	1
	Rings, rubber, test tube	A supply
Fig. 6	Rod, glass, flat-headed	1
	Rods, glass, platinum wire hook	6
	Scoop, aluminium	1
Fig. 10	Screen, burner for water bath	1
	Sieve, rectangular, tinned-brass wire	1
Fig. 8	Sieves with lid and base, circular, brass	A set
	Spatula, horn	1
	Stand, heat test tubes	1
Fig. 10	Stand, water bath	1
	Stoppers, rubber, perforated	A supply
	Thermometers, glass, and wood case	2
	Trays, aluminium	6
	Tray, cordite knife	1
Fig. 5	Tubes, heat test	A supply
	Tube, standard tint paper	1
	Tubing, rubber, Argand gas burner	A length
	Water, distilled	A supply
	Weights, gramme and forceps in box	A set

Specification of Materials

Specification A. Acid, Acetic.—The acetic acid is to be clear, colourless, and free from all impurities, and is not to contain less than 96% CH_3COOH. When 1 c.c. of N/10 potassium permanganate solution is added to 100 c.c. of the acetic acid maintained at 15°, the distinctive colour is to remain for not less than 15 minutes.

One drop of the diluted acetic acid—one volume of acetic acid diluted with four volumes of distilled water—when placed by means of a glass rod on freshly-prepared potassium iodide-starch paper is to produce no colour.

Specification B. Chalk, French.—The French chalk is to be equal in colour to the standard sample, and is not to contain more than 0.5% of moisture.

The bulk of the French chalk is to be such that a volume of 50 c.c. will weigh 23.5 ± 1.0 grms. This is to be determined as follows: —a glass funnel, the stem of which is 11 cm. in length, tapering internally from 8 mm. at the top to 5 mm. at the end, is to be clamped vertically above a 50 c.c. cylinder so that the month of the latter is 7 cm. below the lowest point of the funnel. The cylinder is to be 2.5 cm. in internal diameter, with a ground edge. The French chalk is to be poured gradually into the funnel and allowed to flow into the cylinder until the latter overflows. This should take one minute. The surface of the chalk is then to be levelled off, without tapping or shaking the cylinder, by drawing a straight edge over the mouth of the cylinder. The cylinder and contents are then to be weighed.

The fineness of the French chalk is to be such that it will all pass, without rubbing, through a 0.075 mm. wire sieve of 6,400 meshes per square centimetre.

The French chalk is not to contain more than 0.1% of soluble alkali salts calculated as $CaCO_3$. This is to be estimated as follows:

10 grm. of the chalk are to be boiled with 250 c.c. of water for one minute, filtered, washed, and the filtrate titrated with N/10 hydrochloric acid.

The French chalk, when warmed with hydrochloric acid, is not to give off more than 1% and not less than 0.25% of carbonic acid gas.

The French chalk is not to absorb more than 0.5% of moisture after being dried at 100° till constant in weight, and then exposed under a bell-jar to a saturated atmosphere at 15° to 20° for 24 hours.

Note.—Before use in heat test experiments the French chalk is to be carefully washed with distilled water, dried in a water oven at 65–70°, and exposed to a saturated atmosphere for 24 hours. It is to be kept in a well-stoppered bottle.

Specification C. Glycerin.—The glycerin is to comply with the British Pharmacopœia Specification in all respects.

Specification D (tentative). Paper, Filter.—The paper for making heat test paper is to consist entirely of pure normal cotton cellulose of strongly resistant quality and free from any loading or sizing.

During manufacture, the paper is not to be submitted to artificial heat of any kind.

The paper is to have a smooth white surface, and both sides are to be as nearly alike as possible.

The average length of the fibres is to be 2 ± 0.5 mm.

Ten sheets, when measured with a Ciceri Smith's patent fixed pressure micrometer, are to have a thickness of 1.8 ± 0.2 mm.

The weight of the paper per cubic centimetre is to be . . . gram.

The last treatment in its preparation is to be a thorough washing with pure distilled water and subsequent air-drying in a pure atmosphere.

The paper is to be free from all traces of chemical or other impurity, particularly acids, chlorine and peroxides.

The ash in the paper is not to exceed . . . per cent.

On boiling with 3% caustic soda solution for 60 minutes, the paper is not to lose more than 75.% of its weight.

When heated for 15 minutes at 100° with Fehling's solution, diluted with twice its volume of boiling water, it is not to produce more than 1.25% of its weight of cuprous oxide (Cu_2O).

It is to be supplied in sheets 50 cm. long by 15 cm. wide, and each 100 sheets packed separately in a hermetically sealed tin case closed by a tear-off strip.

For use in the extraction of nitroglycerin from dynamite it is to be supplied in circles 5.5. cm. in diameter, each 100 papers being packed separately.

Papers, Standard Tint.—The standard tint papers are to be made by the method described in, and are to conform to the conditions laid down below.

Specification E. Papers, Test.—The papers are to be prepared by the method laid down below, and are to be tested by the method given in the memorandum.

II. Preparation of the Sample to Be Tested

All the operations in preparing a sample for testing are to be carried out as expeditiously as possible, avoiding exposure to light, as far as practicable, and the test is to be carried out as soon as the sample is prepared.

In weighing out heat test quantities, an accuracy of ±0.05 grm. is sufficient. These quantities are to be weighed out into test tubes which have been fitted with rubber rings, the lower surface of which coincides with the bottom line etched on the test tube.

Explosives of Class 3, *Nitro-compound, Division* 1:

1. *Dynamite and other nitroglycerin preparations from which the nitroglycerin can be conveniently extracted with water in the manner described for dynamite:*

(*a*) The 5.5 cm. glass funnel is to be placed in a hole of the heat test tube stand and a 5.5 cm. filter paper, folded in the usual way placed in it.

(*b*) A cartridge of the sample to be tested is to be opened at one end and rotated with one hand, while with the other the contents of the cartridge are to be loosened by means of pressure between the thumb and forefinger. The first half inch of the sample so loosened is to be rejected.

(*c*) The cartridge is then to be inverted over the scoop, and the loosening operation continued so as to transfer a portion of the explosive to the scoop.

(*d*) When the weight of the sample in the scoop has been adjusted to 13 grm., the sample is to be transferred to the funnel and pressed down fairly tightly with the flat-headed glass rod until the surface is level.

(*e*) The funnel is then to be placed in the heat test tube supported in the heat test tube stand and filled up with distilled water. The stem of the extraction funnel is not to touch the side of the heat test tube.

(*f*) When 2 c.c. of nitroglycerin have been collected in the test tube the extraction funnel is to be removed. The sample is then ready to be heat tested.

(*g*) In the event of any water going through with the nitroglycerin a fresh sample of dynamite is to be extracted.

2. *Carbonite, Monobel Powder, and similar friable nitroglycerin preparations from which the nitroglycerin cannot be conveniently extracted with water:*

(*a*) A cartridge of the sample to be tested is to be opened at one end and rotated with one hand, while with the other contents of the cartridge are to be loosened by means of pressure between the thumb and forefinger. The first half inch of the sample so loosened is to be rejected.

(*b*) The cartridge is then to be inverted over the scoop and the loosening operation continued so as to transfer a portion of the explosive to the scoop.

(*c*) When the weight of the sample in the scoop has been adjusted to 3.2 grm., the sample is to be transferred by means of the aluminium funnel, to a heat test-tube, collected at the bottom by gently tapping the side of the tube with the fingers, and pressed down to a height of 3 cm. by means of the flat-headed glass rod. The sample is then ready to be heat tested.

3. *Blasting Gelatin, Gelatin Dynamit, Gelignite, and Analogous Preparations:*

(*a*) The wrapper of the cartridge is to be opened out and half an inch of the sample is to be removed with the spatula and rejected. A piece weighing 3.2 grm. as nearly as can be judged is then to be cut off for the test. The sample is to lie on its own wrapper during these operations, and direct contact of the operator's hands with the sample is to be avoided.

(*b*) The portion of the sample removed is to be weighed in the scoop and pieces added to, or removed from, it until 3.2 grm. are obtained. This quantity is then to be transferred to the mortar. 6.5 grm. of French chalk are to be weighed out, using the spatula and scoop, and also transferred to the mortar.

(*c*) The sample is to be incorporated with the French chalk by repeatedly squeezing it with the end of the pestle, until it is in a condition in which it can be ground. The times for normal samples should generally be as follows:

Blasting gelatin	11 minutes.
Gelatin dynamite	1 minute.
Gelignite and similar explosives containing less than 63% of nitroglycerine	½ minute.

The mixture is then to be ground by a circular movement of the pestle for a further period of half a minute, and should then be homogeneous in appearance.

(*d*) The mixture is to be transferred to a test-tube by means of the horn spatula and the aluminium funnel, and gently pressed down to a height of 5 cm. with the flat-headed glass rod. The sample is then ready to be heat tested.

(*e*) The pestle and mortar after each grinding are to be thoroughly washed with tap water, rinsed with distilled water, dried with a clean towel, and finally dried in a bath at 100°. The pestle and mortar are to be allowed to cool to the ordinary temperature before being used again.

4. *Cordite, Ballistite and Other Propellants of Class* 3, *Nitro-compound Division* 1:

1. *Explosives in the form of sticks or tubes:*

(*a*) The operator is to wash his hands carefully, thoroughly rinse them in distilled water, and dry them with a clean towel.

(*b*) The sticks or tubes to be tested are to be wiped with clean filter paper.

(*c*) The sample is to be reduced to a condition suitable for grinding in the cordite mill by being cut into small pieces about one-eighth inch long by means of the cordite knife, half an inch being rejected from each end of the sticks or tubes to be tested.

(*d*) The set of sieves with the lid removed is to be placed under the mill so as to allow the ground material to fall directly on to the top sieve.

(*e*) The cut sample is to be transferred from the cordite tray to the mill and ground. The first portion passing through the mill is to be rejected. A sufficient quantity of the sample is to be taken to ensure that enough material is obtained on the second sieve without grinding the whole quantity introduced into the mill.

(*f*) The lid is to be replaced on the set of sieves and the sample is to be sieved for one minute. The material which remains on the second sieve is to be taken for heat test, except in the case of powder in sticks or tubes, the nominal diameter of which is less than 0.03 in.; in this case, the material in the bottom compartment is to be taken for heat test.

(*g*) 1.6 grm. of the ground and sieved sample are to be weighed out in the scoop, transferred by means of the aluminium funnel to a heat test tube and collected at the bottom by gently tapping the side of the tube with the fingers. Three such test quantities are to be so weighed out. The sample is then ready to be heat tested.

(*h*) The set of sieves and the cordite mill are to be cleaned with the cleaning brush before and after the preparation of each sample.

2. *Explosives in the form of grains for small arms:*

(*a*) 1.6 grm. of the sample is to be weighed out in the scoop, transferred by means of the aluminium funnel to a heat test tube and collected at the bottom by gently tapping the side of the tube with the fingers. Three such test quantities are to be weighed out. The sample is then ready to be heat tested.

Explosives of Class 3, *Nitro-compound, Division* 2:

1. *Nitro-cellulose Pulp:*

(*a*) The operator is to wash his hands carefully, thoroughly rinse them with distilled water, and dry them with a clean towel.

(*b*) Six thicknesses of filter paper are to be laid on top of one another. Sufficient of the sample to be tested, to give about 5–6 grm. after the final pressing, is to be spread on the top sheet. Six other thicknesses of filter paper are to be similarly laid over the sample. The whole is then to be placed under pressure as, for instance, in a hand screw press, and pressure applied for three minutes. On removal from the press, the sample is to be rubbed up by hand on the filter paper and again pressed for three minutes on fresh filter paper. The sample is then to be transferred to the rectangular sieve and rubbed through it with the hand.

(*c*) 5 grm. of the sieved sample are to be weighed out in the scoop and spread evenly on an aluminium tray.

(*d*) The oven is to have been brought to, and is to be maintained at, a temperature of 120° F. (48.9°). The tray is to be placed in the oven and kept there for 15 minutes with the door closed.

(*e*) The tray is to be removed from the oven and the sample transferred to the top sieve of the set of sieves. The lid is to be replaced, and the sample sieved for two minutes. For this operation the second sieve is not to be used.

(*f*) The portion of the sample which passes through the top sieve is again to be spread evenly on an aluminium tray and exposed to the air of the room for four hours.

(*g*) 1.3 grm. of the exposed sample are to be weighed out in the scoop and transferred by means of the aluminium funnel to a heat test tube. Two such test quantities are to be so weighed out. The material in each is to be gently pressed down with the flat-headed glass rod to a height of three centimetres. The sample is then ready to be heat tested.

(*h*) The wire sieve and the set of sieves are to be cleaned with the cleaning brush before and after each sample has been sieved.

2. *Compressed Guncotton for Torpedo Warheads and Mines:*

(*a*) About 10 grm. of guncotton are to be removed from the centre of the primer or slab by scraping with the horn spatula.

(*b*) The scrapings so obtained are to be placed in the glass beaker two-thirds full of cold distilled water. The sample is to be frequently stirred up in the water during 15 minutes with the flat-headed glass rod, and then allowed to settle. The water is to be poured off and replaced by a similar quantity of distilled water in which the sample is to be frequently stirred up as before during 15 minutes. After settling, the second wash water is to be poured off.

(*c*) The operator is to wash his hands carefully, thoroughly rinse them with distilled water, and collect the sample by hand—squeezing out the excess of water.

(*d*) Six thicknesses of filter paper are to be laid on top of one another. The washed guncotton is to be spread on the top sheet. Six other thicknesses of filter paper are to be similarly laid over the sample. The whole is then to be placed under pressure as, for instance, in a handscrew press, and pressure applied for three minutes. On removal from the press, the sample is to be rubbed up on the filter paper by hand and again pressed for three minutes on fresh filter paper. The sample is then to be transferred to the rectangular sieve and rubbed through it by hand.

(*e*) 5 grm. of the sieved sample are to be weighed out in the scoop and spread evenly on an aluminium tray.

(*f*) The oven is to have been brought to, and is to be maintained at, a temperature of 120° F. (48.9°). The tray is to be placed in the oven and kept there for 15 minutes, with the door closed.

(*g*) The tray is to be removed from the oven and the sample transferred to the top sieve of the set of sieves. The lid is to be replaced, and the sample sieved for two minutes. For this operation the second sieve is not to be used.

(*h*) The portion of the sample which passes through the top sieve is to be again spread evenly on an aluminium tray and exposed to the air of the room for four hours.

(*i*) 1.3 grm. of the exposed sample are to be weighed out in the scoop and transferred by means of the aluminium funnel to a heat test tube. Two such test quantities are to be so weighed out. The material in each is to be gently pressed down with the flat-headed glass rod to a height of three centimetres. The sample is then ready to be heat tested.

(*j*) The wire sieve and the set of sieves are to be cleaned with the cleaning brush before and after each sample has been sieved.

3. *Tonite and analogous compressed nitro-cellulose preparations:*

(*a*) The operator is to wash his hands carefully, thoroughly rinse them with distilled water, and dry them with a clean towel.

(*b*) The sample is to be held over the rectangular sieve, and a sufficient quantity for the tests required is to be removed from the centre of the cartridge by scraping with the horn spatula.

(*c*) The explosive on the sieve is then to be rubbed through with the hand, and the sieved material spread evenly on an aluminium tray.

(*d*) The oven is to have been brought to, and is to be maintained at, a temperature of 120° F. (48.9°). The tray is to be placed in the oven and kept there for 15 minutes with the door closed.

(*e*) The tray is to be removed from the oven and the sample transferred to the top sieve of the set of sieves. The lid is to be replaced and the sample sieved for two minutes. For this operation the second sieve is not to be used.

(*f*) The portion of the sample which passes through the top sieve is to be again spread evenly on an aluminium tray and exposed to the air of the room for four hours.

(*g*) 1.3 grm. of the exposed sample are to be weighed out in the scoop and transferred, by means of the aluminium funnel, to a heat test tube. Two such test quantities are to be so weighed out. The material in each is to be gently pressed down with the flat-headed glass rod to a height of three centimetres. The sample is then ready to be heat tested.

(*h*) The wire sieve and the set of sieves are to be cleaned with the cleaning brush before and after each sample has been sieved.

4. *Nitro-cellulose Propellants:*

(1) *Explosives in the form of sticks or tubes:*

(*a*) The operator is to wash his hands carefully, thoroughly rinse them in distilled water, and dry them with a clean towel.

(*b*) The sticks or tubes to be tested are to be wiped with clean filter paper.

(*c*) The sample is to be reduced to a condition suitable for grinding in the cordite mill by being cut into small pieces about one-eighth inch long by means of the cordite knife, half-an-inch being rejected from each end of the sticks or tubes to be tested.

(*d*) The set of sieves, with the lid removed, is to be placed under the mill so as to allow the ground material to fall directly on to the top sieve.

(*e*) The cut sample is to be transferred from the cordite tray to the mill and ground. The first portion passing through the mill is to be rejected. A sufficient quantity of the sample is to be taken to ensure that enough material is obtained on the second sieve without grinding the whole quantity introduced into the mill.

(*f*) The lid is to be replaced on the set of sieves and the sample is to be sieved for one minute. The material which remains on the second sieve is to be taken for heat test, except in the case of powder in sticks or tubes, the nominal diameter of which is less than 0.03 in.; in this case, the material in the bottom compartment is to be taken for heat test.

(*g*) 1.6 grm. of the ground and sieved sample are to be weighed out in the scoop, transferred by means of the aluminium funnel to a heat test tube, and collected at the bottom by gently tapping the side of the tube with the fingers. Three such test quantities are to be so weighed out. The sample is then ready to be heat tested.

(*h*) The set of sieves and the cordite mill are to be cleaned with the cleaning brush before and after the preparation of each sample.

(2) *The explosive in the form of grains for small-arms:*

(*a*) A quantity of the sample sufficient for the tests required is to be spread evenly on an aluminium tray.

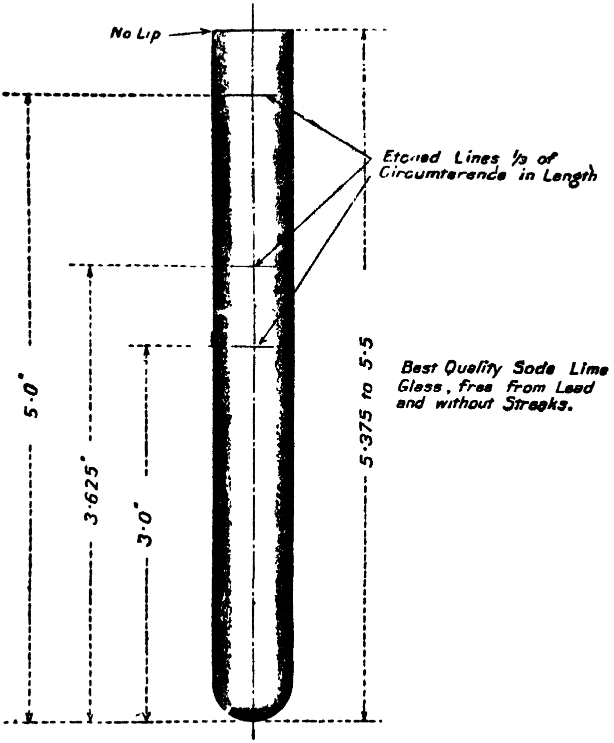
(*b*) The oven is to have been brought to, and is to be maintained at, a temperature of 120° F. (48.9°). The tray is to be placed in the oven and kept there for 15 minutes, with the door closed.

(*c*) The tray is to be removed from the oven and exposed to the air of the room for 4 hours.

(*d*) 1.3 grm. of the exposed sample are to be weighed out in the scoop and transferred by means of the aluminium funnel to a heat test tube. Three such test quantities are to be so weighed out. The sample is then ready to be heat tested.

5. *Ammonite, Bellite, Roburite and Analogous Preparations:*

(*a*) A cartridge of the sample to be tested is to be opened at one end and rotated with one hand, while with the other the contents of the cartridge are to be loosened by means of pressure between the thumb and forefinger. The first half inch of the sample so loosened is to be rejected.


No Lip
Etched Lines 1/3 of Circumference in Length
Best Quality Soda Lime Glass, free from Lead and without Streaks.
5.0"
3.625"
3.0"
5.375 to 5.5

Tubes after Subjection for 3 Hours to a Steam Pressure of 50 lbs. per square inch and then Air dried, must not show more Cloudiness than the Standard Sample so treated. To carry out this Test, the Tubes are to be placed in an inverted position in an Autoclave and well clear of the Liquid.

FIG. 28.—Heat test tube.

(*b*) The cartridge is then to be inverted over the scoop and the loosening operation continued.

(*c*) When the weight of the sample in the scoop has been adjusted 1.3 grm. the sample is to be transferred by means of the aluminium funnel to a heat test tube, and collected at the bottom by gently tapping the side of the tube with the fingers The sample is then ready to be heat tested.

Explosives of Class 4, *Chlorate Mixture, Divisions* 1 *and* 2:

Explosives of this class containing nitro-compounds are to be prepared for the heat test as if they belonged to Class 3.

III. Application of the Test

(*a*) The water bath is to be fitted up as shown in Plate No. 38, and is to be levelled and filled with water up to the outflow. It is to be placed on a table of convenient height in such a position that the heat test tint can readily be observed by reflected light. No part of the apparatus is to be exposed to direct sunlight.

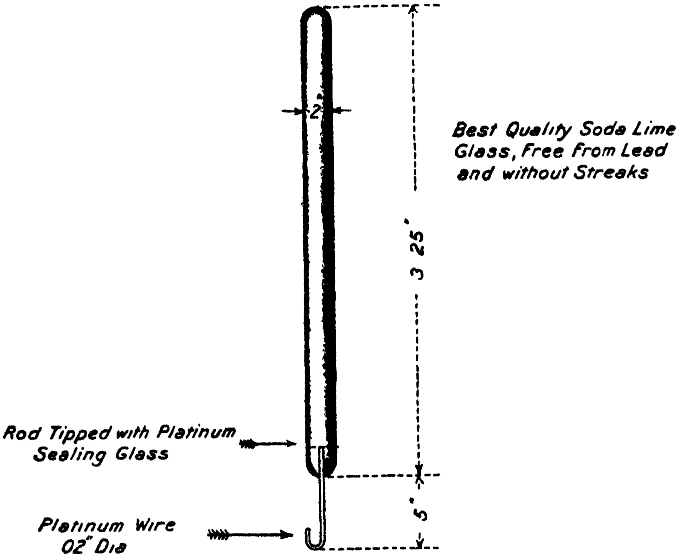

2
3.25"
.5"
Best Quality Soda Lime Glass, Free From Lead and without Streaks
Rod Tipped with Platinum Sealing Glass
Platinum Wire .02" Dia

FIG. 29.—Glass rod with platinum hook.

(*b*) The thermometer, fixed in the rubber stopper, is to be inserted in the wire cage provided for the purpose on the under side of the lid of the water bath to a depth of 3 in. The water is to be heated to the required temperature and maintained at a constant temperature and depth. The temperatures for the various explosives are given in Table I.

(*c*) The glass rod with platinum wire hook is to be inserted in the rubber stopper. A test paper is then to be removed from the brown

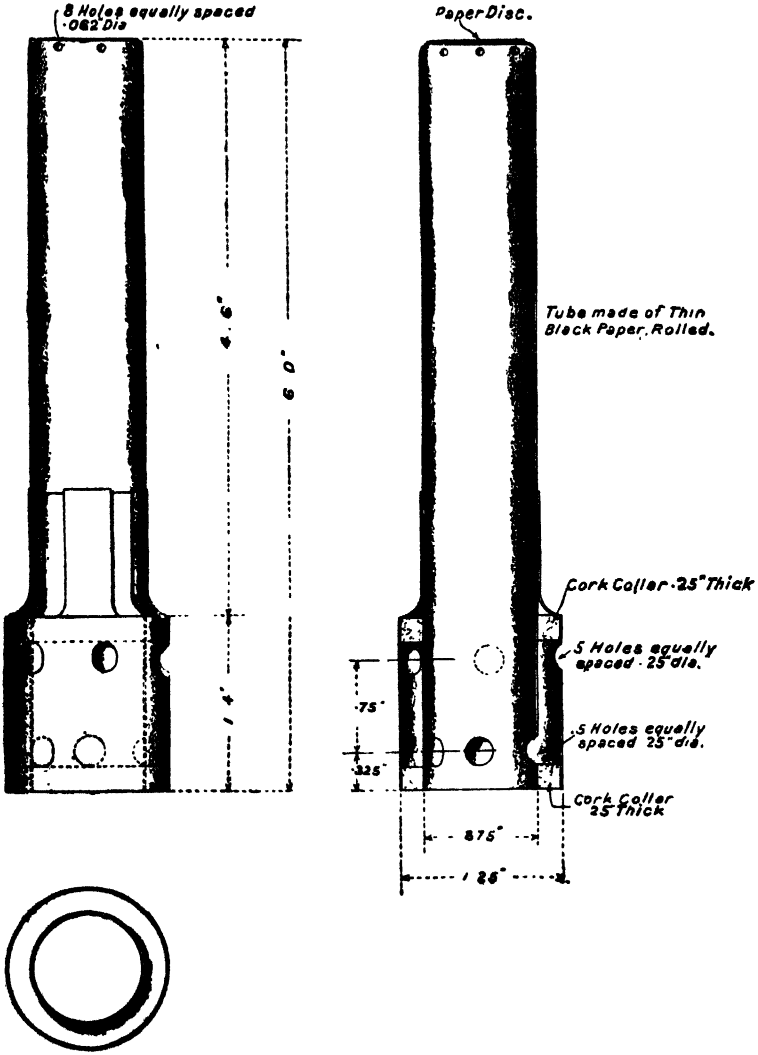

8 Holes equally spaced ·062 Dia
Paper Disc.
4·6"
6·0"
1·4"
Tube made of Thin Black Paper, Rolled.
Cork Collar ·25" Thick
5 Holes equally spaced ·25" dia.
·75"
·325"
5 Holes equally spaced ·25" dia.
Cork Collar ·25" Thick
·875"
1·25"

FIG. 30.—Cap for heat test-tube.

glass bottle by means of the forceps, placed on the glass plate so that its edges coincide with the lines on the plate, and pierced by passing the needle through the paper and the hole in the plate. The test paper is then to be held by means of the forceps, and a mixture of equal volumes of distilled water and glycerin is to be applied to the upper edge of the test paper by means of the glass rod of the dropping bottle in sufficient quantity to moisten the upper half of the test paper by the time the test is complete. The platinum wire hook of the glass rod is then to be passed through the hole in the paper. At no time is the operator to touch the paper with his fingers.

(*d*) The rubber stopper carrying the glass rod and test paper is at once to be firmly pressed into the test-tube containing the explosive to be tested, until the bottom of the stopper coincides with the top line etched on the test-tube, and the position of the glass rod is to be adjusted so that the lower edge of the wet portion of the test paper, which edge is to be approximately horizontal, coincides with the middle etched line on the test-tube. The test-tube is then to be inserted in one of the wire cages of the lid of the water bath, so that the bottom line etched on the test tube coincides with the upper surface of the lid. The rubber ring is to be pressed down on to the bath, and the cap placed in position over the tube.

The quantities of the various explosives to be placed in the test-tube are given in Table I.

The test paper is not to be inspected by lifting the cap until shortly before the time the explosive ought to stand the test as given in Table I.

(*e*) The test is completed when the faint brown line which after a time makes its appearance at the margin between the wet and the dry portions of the test paper, equals in depth of tint the brown line on the standard tint paper.

For any given explosive to pass the test, the time elapsing between the introduction of the tube into the bath and the production of a tint equal to the standard must not be less than the time given in Table I.

After the test is finished, the explosive is to be carefully removed from the tubes, and the tubes thoroughly washed out with tap water by means of the test-tube brush. They are then to be rinsed out and allowed to drain for a few minutes. The washing is repeated with distilled water, the tubes rinsed, allowed to drain, and finally dried in a bath at 100.° The tubes are to be allowed to cool to the ordinary temperature before being used again.

TABLE I

Explosive			Temperature of heat test bath, ° F.	Quantity of explosive heat tested	Time explosive should stand the test, min.
Class	Division	Nature			
3	1	Nitroglycerin extracted from dynamite, etc., by displacement with water.	160 (71.1° C.)	2 c.c.	15
		Carbonite, monobel and similar friable nitroglycerin preparations from which the nitroglycerine cannot conveniently be extracted by water	160 (71.1° C.)	3.2 grm.	7
		Blasting gelatin, gelatin dynamite and analogous preparations.	160 (71.1° C.)	3.2 grm. +6.5 grm. French chalk	10
		Cordite,[1] ballistite and other propellants of Class 3. Division 1.	160 (71.1° C.)	1.6 grm.	10
3	2	Nitro-cellulose pulp, compressed guncotton, tonite and analogous compressed nitro-cellulose preparations.	170 (76.7° C.)	1.3 grm.	10
		Nitro-cellulose propellants.......	170 (76.7 °C.)	1.3 grm.	10
		Ammonite, bellite, roburite and analogous preparations.	170 (76.7 °C.)	1.3 grm.	10

[1] For the acceptance of new cordite and cordite M D. supplied for His Majesty's Naval and Military Services, the details are fixed by the Admiralty and War Office as follows:

		Cordite and cordite M.D.......	180 (82.2° C.)	1.6 grm.	30

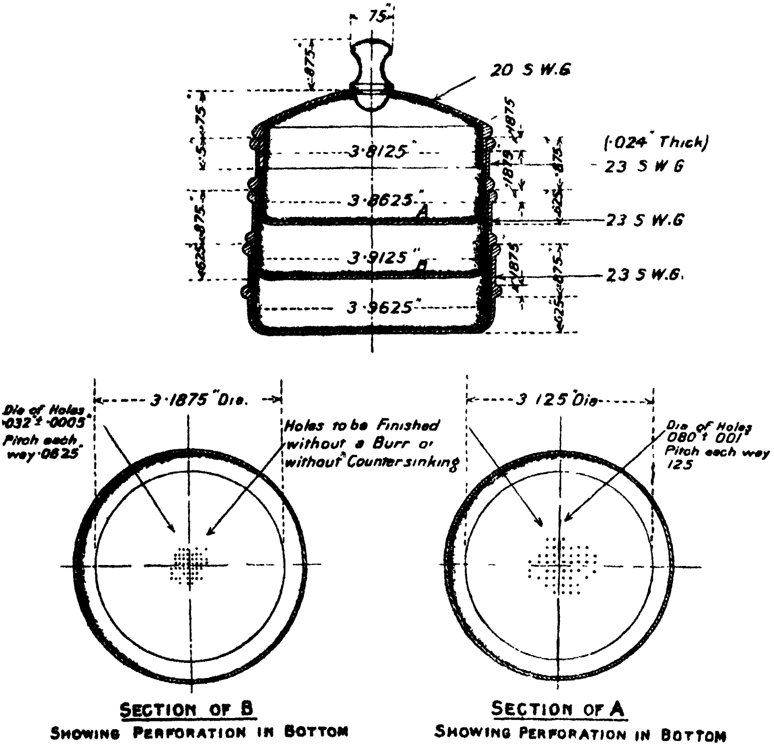
Preparation of Standard Tint Papers

0.48 grm. of the finest yellow ochre, 0.2 grm. of raw umber and 5 grm. of fine white gum arabic, all of which have been very finely ground in an agate mortar, are weighed into a stoppered bottle of about 150 c.c. capacity and 100 c.c. of water added. The whole is shaken in the cold until the gum is dissolved. The suspension is then well shaken and allowed to stand for 1 hour.

A stylographic pen is then filled from the centre of the suspension and, with the aid of a ruler, lines are drawn at a steady pace across one side of a sheet of filter paper to Specification D. The sheet is then cut up into rectangular strips 1 cm. broad by 2 cm. long, each with a line across the middle perpendicular to the length of the strip. The breadth of the line must be not less than 0.5 mm. nor more than 1 mm.

In order to maintain continuity as regards depth of tint, strips in which the tint does not correspond with that of the sealed pattern are to be rejected.

The standard pattern is prepared by and deposited with H. M. Inspectors of Explosives at the Home Office, and will be renewed at intervals not exceeding two years.



SECTION OF B
SHOWING PERFORATION IN BOTTOM

SECTION OF A
SHOWING PERFORATION IN BOTTOM

FIG. 31.—Nest of sieves.

Preparation and Testing of Heat Test Papers

Preparation

Potassium Iodide.—The purest potassium iodide obtainable commercially is to be purified by triple re-crystallisation from pure ethyl alcohol, diluted by the addition of one-twentieth of its volume of distilled water. The crystals are to be kept as small as possible, and are to be spread out on clear filter paper, resting on a glass plate, and allowed to dry in the dark. When dry, they are to be placed in a thin layer on the bottom of a platinum crucible and heated to a dull red heat for one minute over a spirit lamp burning pure alcohol.

When cold, the crystals are to be transferred to a brown glass stoppered bottle, from which the quantities required are to be weighed out.

The potassium iodide used for each batch of filter paper is to be prepared as above immediately before use.

Starch.—The starch used is to be the best maize starch in the form of corn-flour. It is to be purified immediately before use by washing six times by decantation with freshly distilled water. It is then to be placed on a porous plate of unglazed porcelain, allowed to dry in a warm atmosphere in the dark, and stoppered in a brown glass bottle from which the quantities required are to be weighed out.

Preparation of the Dipping Solution.—220 c.c. of freshly distilled water are to be placed in a Jena glass flask and raised to boiling point over a spirit lamp burning pure spirit. 3 grm. of the starch, prepared as above, are to be suspended in 30 c.c. of distilled water, and the mixture poured into the 220 c.c. of boiling water, with continuous shaking. The whole is to be kept boiling gently, and shaken occasionally for 5 minutes. The solution of starch so prepared is to be added to a solution of 1 grm. of the purified potassium iodide in 250 c.c. of freshly distilled water, and the solution well mixed. The mixture is to stand overnight in a dark room. The following day, the clear supernatant liquid is to be carefully siphoned off and used immediately for dipping the paper.

If it is desired to dip a large batch of paper, the foregoing quantities may be multiplied in order to obtain sufficient solution.

Dipping the Papers.—The clear potassium iodide and starch solution is to be poured into a porcelain tray, which is to be kept exclusively for this operation. Sheets of filter paper to Specification D are to be passed through it singly, so that all except 3 cm. at the end of the strip of paper, passes beneath the surface of the liquid.

The strip of paper is to be held above the tray by the dry portion, and a glass rod passed down each side to remove the excess of solution. It is then to be suspended by the undipped portion in a warm dark room, cupboard, or oven until dry.

It is advisable to nip a small piece out of the edge of each sheet at the boundary line between the wet and dry portions as a guide in subsequent cutting.

Cutting and Trimming the Test Paper.—In cutting and trimming heat-test paper the operator is to wear clean cotton gloves.

When the sheets are dry they are to be trimmed by cutting off the unclipped end about 0.5 cm. below the edge of the undipped portion. 0.5 cm. strips are also cut from the other three edges. The sheets are then to be stored in amber-coloured glass jars, kept in the dark.

When a batch of paper has been passed for issue the sheets are to be cut up into rectangular pieces 1 cm. by 2 cm., and are to be issued in this form.

All the above operations are to be carried out in a building specially reserved for this work. This building is to be protected from the direct access of the sun's rays, and is, as far as possible, to be kept dark.

It will be noticed that the weight of the paper per cubic centimetre and the ash were not actually settled by the Committee, and in this as in a number of other important details the test as carried out by the British War Office differs from the Home Office test. One of the principal objects of the enquiry, the unification of the methods, has not therefore been attained. The War Office methods are given in Appendix I of "Pamphlet No. 7, Regulations for Army Ordnance Services, Part II" (H. M. Stationery Office, 1920, price 6d). In India the military rules for carrying out the heat test are the same as in England, but for civil explosives the "Memorandum" has not yet been adopted and the rules in force are the older ones of the Home Office as given in the previous edition of "Allen."

United States Directions for the Heat Test

The regulations issued by the military and naval authorities of the United States differ considerably from the English ones: in some respects they are more explicit, in others less so. They are here given in full:

Blasting gelatin, gelatin dynamite, and analogous preparations are also submitted to liquefaction and exudation tests.

Nitroglycerin.—The water-bath of the potassium iodide and starch testing-apparatus is brought to 160° F. (71.1°), and maintained at that temperature, being regulated by the thermometer which should be immersed about 2¾ in. in the water. The source of heat should be carefully watched, and at no time should the temperature of the bath rise or fall more than 1° F. from 160° F. 50 grains of nitroglycerin are placed in each test-tube and carefully weighed, being careful not to get any on the sides of the test-tube; this may be done by using a suitable dropper or glass tube.

A piece of test-paper is taken with the pincers and laid down on a piece of clean filter-paper. The test-paper is held in place by the end of a glass rod which has been thoroughly cleaned, heated, and cooled. A small hole is made in the test-paper with the point of the pincers opposite the middle of one end of the paper and about 0.2 in. from the edge. The test-paper is taken up with the pincers, the platinum hook inserted through the hole just made, the hook bent with the pincers until the throat of the hook is closed tightly on the paper so that it will stand stiffly up when the paper is held vertically above the glass rod. The glass rod with test-paper is placed carefully aside under a bell glass or other protecting cover where it will be protected from fumes and dust. In the same way the other test-papers are prepared.

A solution of pure glycerol and distilled water, in equal volumes, is prepared.

One of the test-papers is taken, held with the paper up, and a drop of the glycerol solution is placed on each of the lower corners of the test-paper, as held, the paper should absorb this evenly about halfway to the opposite upper edge, leaving a distinct line about midway between the moistened and the unmoistened parts. One of the test-tubes is placed in the bath through one of the apertures in the cover and is immersed until the sample is below the surface of the water. The test-paper, moistened with glycerol, is placed in the test-tube, and the glass rod is moved through the cork until the line between the moistened and unmoistened parts of the test-paper is about $5/8$ of an in. above the upper surface of the cover. This time is recorded. The same is done with each of the other 2 test-papers. The line between the moistened and unmoistened parts of each test-paper is watched carefully, and the exact instant that a faint brown colour[1] appears on this line of demarcation on each test-paper is recorded. This completes the test.

The nitroglycerin under examination will not be considered "thoroughly purified" unless the time elapsed between the insertion of the test-paper and the appearance of the brown colour is at least 15 minutes. The average of the records of all the tubes will be taken.

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[1] In order to detect this colour promptly, the water-bath should be so placed that a bright reflected light falls on the papers.

Explosive Gelatin.—If explosive gelatin is under examination a sample ot 50 grains is intimately incorporated with 100 grains of French chalk, using a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, should be thoroughly washed with distilled water, dried in a water-oven, and then exposed to moist air under a bell jar until it has taken up about 0.5% of moisture. It should then be placed in a glass-stoppered jar for use.

Each test-tube is filled with this mixture to a depth of 1¾ in., the tube being gently tapped on a table to insure a proper degree of settling.

The heat test is then conducted as explained for nitroglycerin. Explosive gelatin will not be considered as serviceable unless the average time of the test is at least 10 minutes.

Explosive gelatin is subjected also to a liquefaction and exudation test as follows:

Liquefaction Test of Explosive Gelatin.—A cylinder is cut from the cartridge having its height equal to its diameter, care being taken to have the ends cut flat and true.

This cylinder is placed on a piece of filter-paper on a smooth clean board, and secured to the board by an ordinary pin forced through it along its axis into the board.

It is exposed in this condition for 144 consecutive hours to a temperature ranging from 85 to 90° F.

The original height of the cylinder should not decrease more than ¼, and the upper cut surface should retain its flatness and sharpness of edge.

Exudation Test of Explosive Gelatin.—There should be no separation of nitroglycerin in the liquefaction test or under any conditions of storage, transport, or use, or when the explosive is subjected three times in succession to alternate freezing and thawing.

Loose-fibre Guncotton.—The material is dried at a temperature not greater than 40° to constant weight; then exposed on trays to the air in a room free from fumes, until from 1 to 2% of moisture has been absorbed. It is then gently rubbed through a ten-mesh sieve to insure uniformity of division, being careful that it does not come in contact with the hands or any piece of apparatus not perfectly free from any trace of acid or alkali. 1.3 grm. are weighed out and placed in a test-tube 5½ to 6 in. long and not less than ½ in. internal diameter.

The potassium iodide and starch test is conducted as explained for nitroglycerin except that the water-bath is heated to 150° F. (65.5°). The test-papers, prepared as already explained, are inserted in the test-tubes[1] and the papers adjusted in the tubes so that the line dividing the dry and moist portions of the test-paper is on a level with the lower edge of the film of moisture which is deposited on the side of the tube soon after inserting it in the bath.

Nitrocellulose intended for the manufacture of smokeless powder must not show a brown colour in less than 35 minutes at 150° F. (65.5°).

Blocks or Discs.—Guncotton for demolition purposes is issued in the form of compressed pulp in discs or blocks. This form of guncotton is prepared for the heat test as follows:

Sufficient material to serve for 2 or more tests is removed from the centre of a block or disc by scraping, and reduced to a fine powder by rubbing between pieces of clean, dry filter-paper. This is spread out in a thin layer upon a paper tray about 6 by 4½ in., which is then placed inside a water-oven, kept as nearly as possible at 120° F. for 15 minutes, the door of the oven being left wide open. The tray is then removed and exposed to the air of the room for 2 hours; during this time the material is rubbed on the paper tray with a clean glass rod and reduced to a fine and uniform state of division.

The test is carried out otherwise in the same manner as for loose fibre guncotton and the temperature of the bath is the same, 150° F.

There should be no brown tint within 10 minutes.

Poacher Sample.—In case the sample is taken during the manufacture of nitrocellulose, it is taken after the poaching and after having been thoroughly washed in pure cold water. The sample is pressed dry in a hand press and rubbed in a clean cloth until finely divided, care being taken not to let it come in contact with the hands.

Smokeless Powder.—The sample should be prepared by cutting into slices 0.02 in. thick. These slices are exposed to the air for at least 12 hours.

The test-tube sample consists of 1.3 grm

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[1] The standard water bath for nitrocellulose holds ten tubes; it is long and narrow to prevent heating the upper part of the tubes as much as possible. Tubes are immersed 2¾ in. in the bath.

The usual potassium iodide test is followed, except that the temperature is considerably higher for simple nitrocellulose powders, being 100° (212° F.) instead of 65.5° (150° F.). Each sample must stand this temperature without showing a brown line for 10 minutes.

Powders containing nitroglycerine should stand the test at 65.5° for 20 minutes.

Precautions

It is of the utmost importance that all the operations connected with the Abel and other trace tests be conducted in a room that is quite free from acid fumes, as the test is affected by very minute traces of acids and other substances. It has been calculated by Will that the quantity of nitrous acid necessary to affect heat-test paper corresponds to 4×10^{-5} mg. of nitrogen. If heat tests have to be carried out frequently, it is best to keep a special room for the purpose or, better still, a special building remote from any place where acid or other fumes are generated. The operator also must be careful not to introduce anything that can affect the test: he should wash his hands before starting the test and should not wear clothes that can have become contaminated

In 1901, Cullen called attention to the desirability of having a uniform official source for the heat-test papers used throughout the British Empire (*J. Soc. Chem. Ind.*, 1901, **20**, 8), as very trifling differences in the method of preparation affect the results considerably. All contractors for explosives to the Government can now obtain heat-test papers made at the Royal Gunpowder Factory, Waltham Abbey, identical with those used by the War Department inspectors throughout the Empire. The Home Office also supplies heat-test papers to their inspectors and to manufacturers of explosives. Unfortunately, the War Department papers are not the same as those of the Home Office, as they are made from a thicker filter-paper, and are consequently less sensitive. The War Department recommends that the papers be kept for 6 weeks before use but they are actually kept much longer. The United States Government also issues heat-test papers to the manufacturers who contract to supply it with explosives.

If heat-test papers from other than the official source be used, it is necessary to compare them with the official papers as regards sensitiveness. This may be done by having glass rods with two platinum hooks side by side, and hanging on each of them one of the papers to be compared. The heat test is then carried out in the usual way and if there is a small difference in the time in which the standard tint appears, a correction is applied to all the results obtained with the papers in question. If the difference is large, the papers should be discarded.

The objections to the test are due to its extreme sensitiveness. On the one hand, samples that are really stable sometimes give low heat tests, because they have become contaminated with minute traces of some material which is really harmless but affects the iodide and starch paper; ozone, for instance, has a powerful effect. On the other hand, samples of insufficient stability sometimes give high tests, because they contain traces of some substance that interferes with the reaction between the oxides of nitrogen and the paper. Mercuric chloride is a substance of this kind, for an extremely small proportion will lengthen the heat test of the sample very considerably. In Germany it was at one time usual to carry out the final washing of guncotton with water containing a little of this salt ostensibly in order to prevent the growth of fungus on the guncotton, but this object can be better achieved by using phenol, and it seems probable that the real object was to improve the heat-test. At any rate, this is the view that has always been taken by the authorities in England, and they regard the addition of mercuric chloride or any similar masking agent as a most reprehensible practice.

Methods for the detection and estimation of minute traces of mercury and mercury compounds in explosives were given in the 32nd Annual Report of H. M. Inspectors of Explosives, 1907, **17**, Allen's Commercial Organic Analysis, 4th Ed., vol. III, pp. 608–612. They are not repeated here as they seldom have to be applied.

There are many other substances which mask the Abel heat test, and so make the explosives containing them appear much more stable than they really are. Ethyl acetate and alcohol prolong the test powders gelatinised with them, at any rate when they are new. Acetone, on the other hand, has little or no effect on the test. A. Dupré found that the carbonate of calcium and magnesium had no appreciable effect, whereas sodium carbonate prolonged the test of bad samples of explosives with which it had been mixed, but decreased that of good ones (12th Annual Report of H. M. Inspectors of Explosives, 1887, 22). Camphor, aniline, diphenylamine, mineral jelly and many other substances, which react with the oxides of nitrogen, prolong the heat test, but in many cases this prolongation corresponds to a real improvement in the Stability.

In old explosives the masking agents, if originally present, become exhausted, but varying quantities of a large number of decomposition products are present which may affect the test, either lengthening or shortening it. Besides the organic compounds, water, nitric and nitrous acids are among the products and, as they are volatile, they may cause considerable fluctuations in the results according as they are allowed to escape more or less before the test is applied. Oxalic acid shortens the heat test (Bravetta and Parrozzani, Stabilité des Nitrocelluloses, 1908, 17), but probably does not affect the stability greatly.

Significance of Heat Test.—R. Robertson and B. J. Smart have carried out a number of experiments and calculations to ascertain the significance of the results of the Abel heat test in the case of nitroglycerin and ungelatinised gun-cotton (*J. Soc. Chem. Ind.*, 1910, **29**, 130). They found that the quantity of nitric peroxide required to produce the standard tint on the service heat test paper is 135×10^{-6} mg., a figure which is very near that arrived at in the laboratory of the Duneberg Explosives Factory, namely, 4×10^{-5} mg., nitrogen, equivalent to 131×10^{-6} mg. NO_2 (*Mitt. aus der Centralstelle*, Heft 3, S. 28). When the papers are exposed to an unlimited quantity of air containing nitric peroxide, the time required to produce the standard tint is inversely proportional to the concentration of nitric peroxide: for the service papers the product of the time in minutes by the concentration, in mg. of nitric peroxide per c.c., is 31×10^{-6}. From theoretical considerations Robertson and B. J. Smart deduced the equation:

$$T = \frac{KV}{Q} \log \frac{r}{r + \frac{Q^2}{KV^2} - \frac{QrT}{KV}}$$

where Q is the quantity of nitric peroxide required to produce the tint, 135×10^{-6}

K the product of the time into the concentration, 31×10^{-6}

V the unoccupied volume of the heat-test tube, 18 c.c.

r the rate of rise in the concentration of nitric peroxide in the heat test-tube due to decomposition of the explosive.

and T the time.

From the results obtained in the Will test and from other data it is calculated that for good gun-cotton $\log r = .06021\,t - 10.6928$, where t is the temperature in °C. But there is a lag in the time of the test due to the fact that at first the gun-cotton is colder than the bath. The rate of rise of temperature was actually measured by means of a thermo-couple. Taking into consideration the results thus obtained, the time for the heat test of gun-cotton was calculated for different temperatures and compared with those observed:

Temperature °C	r	Time from equation, minutes	Lag, minutes	Calculated time, minutes	Observed time, minutes
70 0	0 332	27 0	4	31 0	28, 29
72 0	0 43	21 5	4	25 5	25, 25½
74 0	0 59	17 0	4	21 0	21, 21½
76 7	0 84	13 0	4	17 0	15
79 5	1 24	10 0	4	14 0	12
82 25	1 81	7 5	4	11 5	11½
100 0	21 26	1 75	4½	6 25	4½

The agreement, taken in conjunction with the results of other experiments, shows that in the case of fibrous gun-cotton the Abel heat test represents the decomposition of the gun-cotton itself during the test, and is not due to dissolved impurities. But with gelatinsed smokeless powders, that have been made some time, this is not the case; the gun-cotton dissolves considerable quantities of nitrogen peroxide, which are not entirely given up again by the comparatively compact material, even when it is exposed to the atmosphere for some days in the ground state. It was found by A. C. Egerton that gun-cotton gave the same length of test when two papers were suspended in the test-tube instead of one (*J. Soc. Chem. Ind.*, 1914, **33**, 113).

The reason why it is necessary to regulate the quantity of moisture in the gun-cotton is that, when very dry, it gives a high test owing to the drying of the test paper, whereas very wet gun-cotton also gives a high test, because the excess of water condenses in the tube and absorbs much of the nitric peroxide.

Since the heat test of a gun-cotton is only a measure of its initial decomposition, the test cannot be regarded as an absolute indication of its stability. In the Will test non-volatile catalysers may not give rise of decomposition until fifteen or thirty minutes have elapsed at a temperature of 135°, and this would correspond to a period of some days at 170° F. (76.7°).

When nitroglycerin is heat-tested in the ordinary way the result obtained is very much higher than would be expected from the known rate of its decomposition, which is more than nine times as rapid as that of gun-cotton.

$$\log r = .06021\,t - 9.7312$$

This is due to the fact that the nitrogen peroxide formed mostly remains dissolved in the liquid, from which it can only escape slowly because but a very small surface is exposed. The result is largely dependent on the amount of oxide of nitrogen that has accumulated in the liquid. If a large surface be exposed by mixing the nitroglycerin with silica wool, the results obtained agree with those calculated.

When small quantities of gun-cotton are added to nitroglycerin, the heat test rises, owing either to the oxide of nitrogen being more soluble in the gun-cotton, or to the increased viscosity of the liquid. When sufficient gun-cotton has been added to break up the surface of the liquid, the heat test falls rapidly, but on account of the felting of the fibres the comminution is never so perfect as when silica wool is used. If the gun-cotton contains sulphuric ester, it greatly accelerates the decomposition of the nitroglycerin and low heat tests are obtained. In the following experiments the gun-cotton A contained 0.15 % of alkaline matter expressed as calcium carbonate, B was neutral, and C contained 0.7 % sulphuric acid as sulphuric acid ester:

%, N/G	%, G/C	Temperature of test	Type of gun-cotton used		
			A, minutes	B, minutes	C, minutes
100.0	0.0	180°	19	14½	19
0.0	100.0	170°	17	17	16
97.5	2.5	180°	31	....	21
95.0	5.0	180°	32	15	30
90.0	10.0	180°	86	38	34
80.0	20.0	180°	28	13	9
70.0	30.0	180°	17	....	6
60.0	40.0	180°	13	6½	4

Other Trace Tests

Zinc Iodide and Starch Test.—In Germany, the Netherlands, and some other countries a modification of the Abel test is used, zinc iodide being substituted for potassium iodide, and it is claimed that the test is thereby rendered more sensitive. This, however, is hardly an advantage, as the principal fault of the Abel test is its excessive sensitiveness. In Spain a paper is used impregnated with a solution containing starch, zinc iodide, and zinc chloride.

Guttmann's Test.—Guttmann carried out a series of experiments to find a reagent which would not be masked by solvents such as ether-alcohol and ethyl acetate nor by such substances as mercuric chloride (*J. Soc. Chem. Ind.*, 1897, **16**, 293). He decided upon a paper impregnated with diphenylamine in sulphuric acid solution. Of the diphenylamine 0.100 grm. is dissolved in 40 c.c. of water, together with 10 c.c. of concentrated sulphuric acid and when cold an equal volume of pure glycerol is added. Filter-paper is well washed, dried and cut into strips 1.0 in. by 0.4 in. One of these strips is suspended from a hook, as in the Abel heat test and the top edge is moistened with 2 drops of the reagent, so that they run together and cover about a quarter of the paper. Otherwise the test is carried out like the Abel test at a temperature of 70°. The moistened part of the paper after a time becomes greenish-yellow and then a dark blue mark appears at the dividing line between moist and dry parts of the paper. This is the end of the test. The test was adopted by the Belgian military engineers and in several other countries, but unfavourable reports have been made by several investigators who have been unable to obtain concordant results with this test.

Spica's Test.—In this test *m*-phenylene-diamine hydrochloride and cane-sugar are used to impregnate the paper. The reagent is much more sensitive than potassium iodide and starch, and for this reason has not been adopted extensively.

Several other "trace tests" have been proposed, but none of them has come into general use.

Fume Tests

Vieille Test.—In this test the explosive is heated in a closed tube with litmus-paper in a specially designed bath. The temperature of the bath is 110°, that of the sample 108.5°. The quantity of explosive taken is 10 grm. preferably in one piece; this is heated in the bath for a day of eight hours or until the litmus-paper has assumed a standard red tint. Next day this is done again with a fresh piece of litmus-paper, and the procedure is repeated until the litmus-paper is reddened in one hour. All the times are then added together and the total time is noted. This test has been adopted officially in France and is also used considerably in other countries, but it is generally considered to be unreliable. (See Sy, *J. Franklin Institute*, 1908, vol. 166, pp. 249, 321, 433.) Thus, in the Report on the Jena Disaster (vol. iii, p. 130) a case is mentioned in which duplicate tests on the same sample taken at different establishments gave results at twenty-two minutes and nineteen hours respectively, and at the same establishment duplicate tests often give very divergent results (vol. iii, pp. 177, 215). Sy ascribes the discrepancies to the difficulty in closing the tubes uniformly tightly.

Powders in naval service are considered dangerous when the test has fallen to fifteen hours, and in military service twelve hours. (Buisson, *Problème des Poudres*, p. 215.) More reliance is now placed in France on the examination of the stabiliser, diphenylamine (Vennin et Chesneau, p. 423).

In Italy a modification of the Vieille test is used devised by Lepidi (E. Bravetta, *Z. ges. Schiessu. Sprengstoffw.*, 1912, 496). The powder is heated daily at 100° for ten hours and aerated for fourteen hours.

German 135° Test.—This is a test which is much used for nitrocelluloses. The following are the particulars of the method as carried out in the United States Ordnance Laboratory (see Sy, *J. Franklin Inst.*, as above, also *J. Amer. Chem. Soc.*, 1903, **25**, 550):

2.5 grm. of the sample to be tested are dried at the ordinary temperature of the laboratory for 12 hours and placed in a strong test-tube. A piece of blue litmus is placed in the tube abut ½ in. above the sample, the paper being folded lightly so as to give the folds sufficient elastic power to hold the paper in place by pressure against the sides of the tube. The tube is lightly closed by a cork with a hole 0.15 in. diameter bored through it, and so placed in a bath of boiling xylol (the b. p. of which is 135°) that only 6 or 7 mm. project above the surface.

Examination of each tube is made each 5 minutes after 20 minutes have elapsed. In making this examination the tube should be withdrawn only ½ its length and quickly replaced.

2 tubes are used in each test, and there must be no failure in either tube.

Three observations are made: (1) Time of complete reddening of litmus-paper; (2) time of appearance of brown nitric oxide fumes; (3). time at which the sample explodes.

Stable explosives should give the following times:

	Litmus not reddened in	No nitric fumes in	No explosion in
Uncolloided nitrocellulose	30 min	45 min	5 hr.
Pure nitrocellulose powder	1 hr. 15 min	2 hr.	5 hr.
Nitroglycerin powders	30 min	45 min.	5 hr.

For the results to have value they should be compared with those of a known stable explosive of the same kind under the same test by the same operator, using the same test-paper.

Temperature of Ignition.—In this test a small quantity of the sample is introduced into a heated test tube and the temperature is observed at which it ignites or decomposes actively. It is not used much for ascertaining the relative stability of different lots of similar explosives, as very different degrees of stabilisation only make slight differences to the temperature of ignition, but it is applied sometimes for classifying different explosives as regards sensitiveness to ignition. It is, however, used in testing celluloid. Under the German regulations the sample of celluloid is cut into small pieces and 0.1 grm. is placed in a test tube which is immersed in an oil bath at 100°. The temperature of the bath is raised 5° a minute until the material suddenly decomposes. The limit for satisfactory samples has been fixed at 150° (W. Will, *Z. angew. Chem.*, 1906, 1377; *Report of Departmental Committee on Celluloid*, 1913, Cd. 7158, 16).

The following is the method adopted in the United States for ascertaining the stability of "pyroxylin plastics" and picture film: The sample is finely divided either with a steel rasp or a pair of scissors according to its thickness. 0.2 grm. is then weighed out into a test tube measuring 5/8 by 5 in. which is closed with a cork. The test tube is then placed vertically in an oil bath at 100° and the temperature is raised 5° a minute until the material decomposes violently or ignites, the oil meanwhile being kept well stirred. This temperature should not be below 160°. Japanese tooth brushes have been found to be made of particularly unstable celluloid and have given rise to a number of fires during transport in America (U. S. Bureau of Explosives Report, 1917, **10**, 27, and subsequent years).

Silvered Vessel Test.—This has been used in the British Service for testing the stability of cordite Mk. I, which has been made for some time and has given low heat tests. Full instructions for carrying it out are given in the "Regulations for Army Ordnance Services, Part II, Pamphlet 7." The cordite is ground as for the heat test and about 50 grm. are placed in a glass flask with a double wall, the space between the walls being evacuated and silvered to reduce the loss of heat. A thermometer is introduced through the neck so that the bulb is in the centre of the powder. The whole is then placed in a thermostat at 80° and observations of the thermometer are taken at regular intervals until decomposition sets in with sufficient activity to raise the temperature of the cordite to 82°. A good

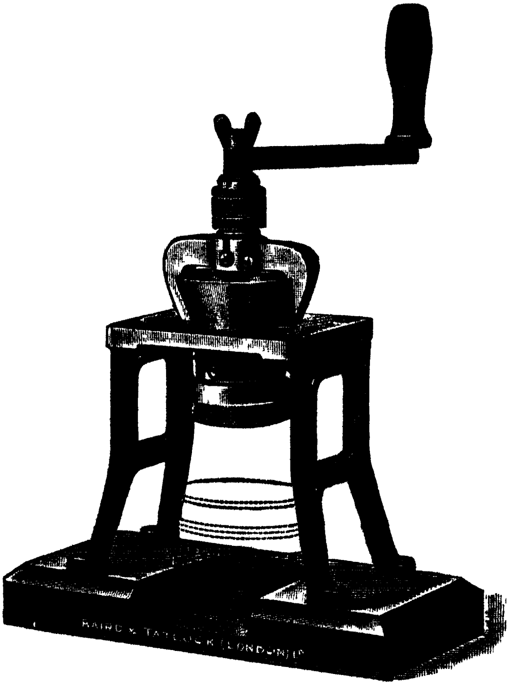

FIG. 32.—Mill for cordite.

cordite will stand the test for 500 hours or more. If the test be below 200 or 300 hours, according to the temperature of storage, the cordite is considered unserviceable.

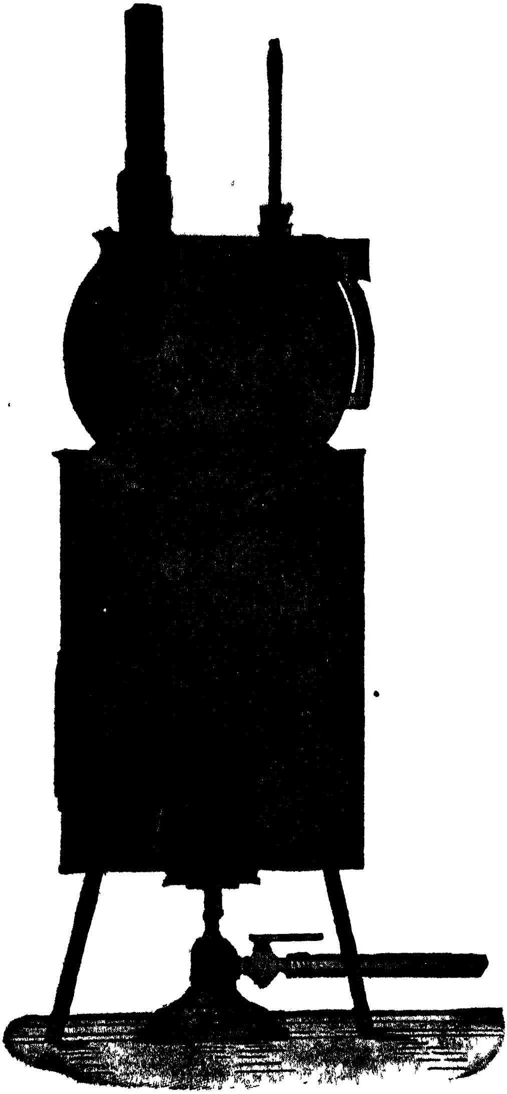

FIG. 33.—Heat test bath assembled.

A number of tests have been proposed in which the explosive is kept at temperatures lower than the above and for correspondingly longer periods. Such tests are, however, unsuited to any but special laboratories and consequently cannot be dealt with in this book. It has yet to be proved that the results obtained are sufficiently reliable to compensate for the cost involved.

QUANTITATIVE TESTS

Will Test.—In the Will test, which is used as a rule only for ungelatinised nitro-cotton, the explosive is heated at a temperature of

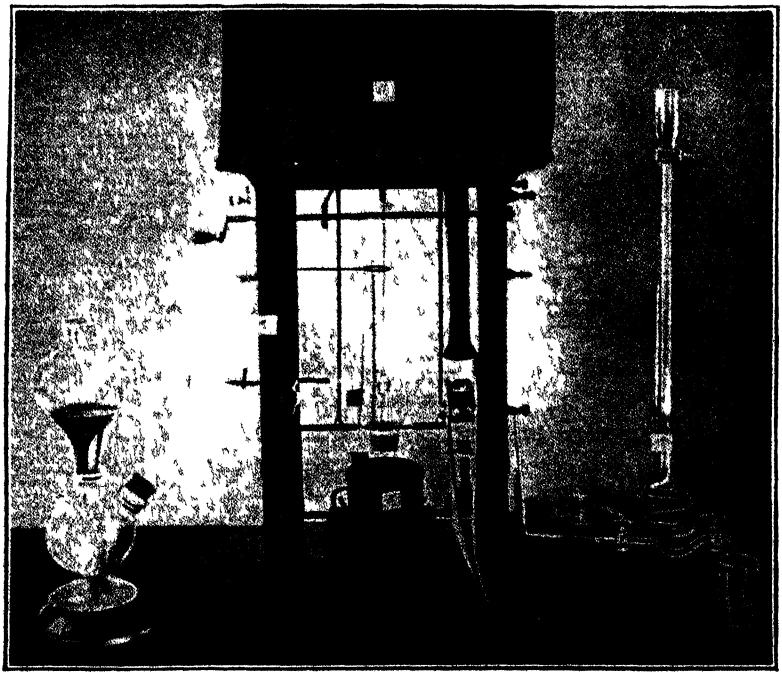

FIG. 34.—Will's test.

135° in a current of dry carbon dioxide, and the nitrogen evolved is measured every quarter of an hour; 2.5 grm. of the dry nitro-cotton are weighed out into the funnel tube into which the carbon dioxide passes through a spiral tube fused on to its lower end

(See Mitteilungen aus der Centralstelle, Heft 2, 1900; Heft 3, 1902; also R. Robertson, *J. Soc. Chem. Ind.*, 1902, **21**, 819). The rate of flow of the gas is rendered apparent by bubbling it through sulphuric acid, which at the same time dries it. Will generated the carbon dioxide in a Kipp's apparatus from marble and hydrochloric acid, using special precautions, to free it from air, but Robertson preferred to take it from cylinders of the compressed gas carefully selected. It may also be generated from sulphuric acid and potassium bicarbonate solution. In any case the gas must be tested, and a correction introduced for the air it contains. From the tube *z* the gases pass to a copper tube *l*, containing metallic copper and copper oxide, which is maintained at a red heat. This destroys all organic gases, converting the carbon and hydrogen into carbon dioxide and water; nitrogen compounds are converted into elementary nitrogen. Hence the gases are led to the measuring tube *G*; this is filled with strong caustic soda solution of specific gravity 1.2; at its lower end there is a zig-zag to facilitate the absorption of the carbon dioxide. Carbon dioxide is passed through the apparatus until all air has been displaced, then the oil-bath *B*, which is kept at 135°, is raised and the test starts. There is a stirrer in the bath worked by a water-motor or other convenient means, and the whole is enclosed in the cupboard *S*, which keeps off draughts and protects the operator in the event of an explosion. Robertson has modified the apparatus in some details; he passes the gas at the rate of 1000 c.c. per hour instead of 1500, the rate used by Will, as he found that the slower rate shows up bad gun-cottons more effectively.

The results given by the test are reliable, provided care be exercised to ensure that the apparatus is air-tight and working properly in all respects. A good gun-cotton evolves nitrogen at a uniform rate; for Service gun-cotton containing about 13% nitrogen Robertson found that the quantity evolved in 4 hours by 2.5 grm. was from 6.5 to 8.5 mg. Nitro-cottons less highly nitrated decompose less rapidly provided they have been stabilied equally well. One reason why the Will test gives such uniform and satisfactory results is, no doubt, that air and moisture are excluded.

Robertson and Napper (*Trans. Chem. Soc.*, 1907, **103**, 761) have carried out experiments with a number of modifications of the test, and have thereby thrown considerable light on the composition of the gaseous products of decomposition, and their reciprocal influence on the decomposition.

Bergmann and Junk Test.—The Prussian military authorities and the German Commission have adopted a test devised by Bergmann and Junk (*Z. angew. Chem.*, 1904, 17, 982). It has the merit of being quantitative and does not require such an elaborate apparatus as the Will test. In this test the gun-cotton is heated in a glass tube at 132°, and the nitrous gases are absorbed in water,

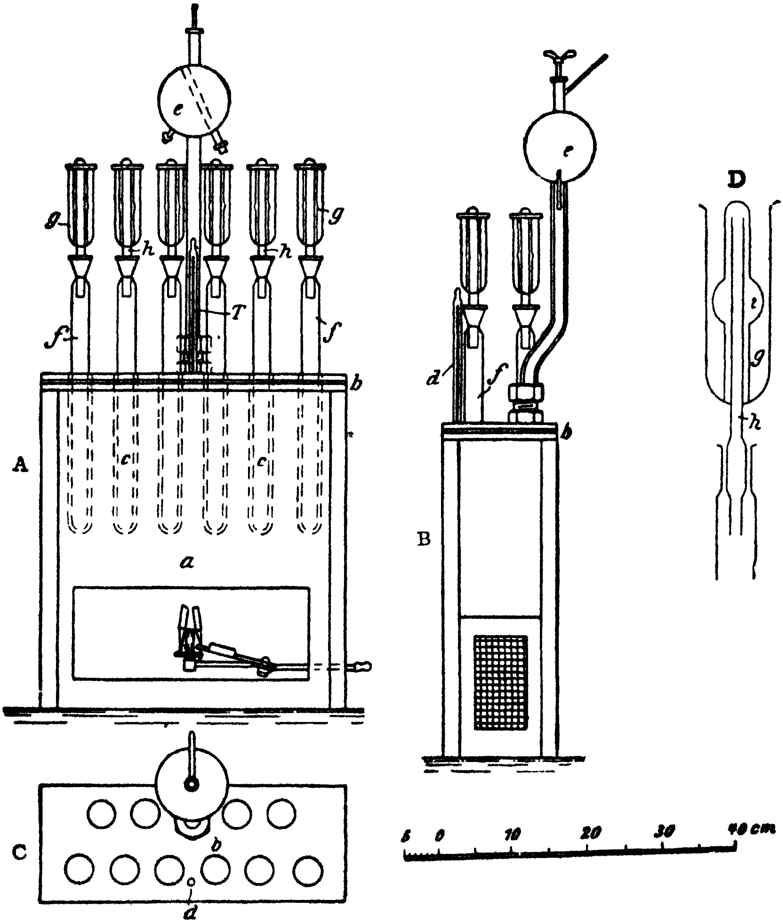

FIG. 35.—Bergmann and Junk's test. *A*, Elevation; *B*, side view; *C*, plan; *D*, beaker absorption apparatus.

and when the heating is finished they are estimated by the Schultze-Tiemann method. The glass tube has thick walls and is 35 cm. long and 2 cm. in internal diameter. Into the neck is ground a hollow glass stopper, which is surmounted by the absorption apparatus shown, D, Fig. 12.

The heating bath is a rectangular copper vessel 35 cm. × 10 cm. × 25 cm. high with ten tubes, each 20 cm. long, let into it to take the glass tubes. It is also fitted with a reflux condenser and a small tube to take thermometer; it is filled with amyl-alcohol, which is kept boiling by means of a burner

In the authors' paper there is a description of an elaborate wooden cup-board to take the testing apparatus, so that in case of an explosion the effects may be confined. It is, however, expensive and greatly increases the danger of fire. A large piece of plate glass should be erected in front of the apparatus with a piece of woven wire before it, and there should be an arrangement of cords and pulleys to enable the operator to remove any tube from the bath without handling it.

The gun-cotton is dried in a bath with a good current of air at a temperature of 40° to 50° for three hours. Then it is passed through a sieve of 2 mm. mesh, and the drying is continued in a vacuum desiccator over sulphuric acid until it contains not more than 1% of water, 2 grm. are weighed out and introduced into the tube, any particles adhering to the sides being removed by knocking the tube or brushing it down with a feather. The glass stopper is slightly lubricated with good mineral lubricating oil and is inserted, the absorption apparatus is half-filled with water, an the glass tube is introduced into one of the holes in the bath, which should be at a temperature of 132°. The heating is continued for two hours or other convenient time, and then the tube is removed from the bath. As the air in the tube contracts the water is drawn out of the breaker *g* on to the cotton. The absorption apparatus is washed out into the tube, and the volume is made up to the 50 c.c. mark, which is on the tube. The liquid is then filtered through a dry filter, 25 c.c. of the filtrate are taken, 1 c.c. of N/2 potassium permaganate solution is added to oxidise the nitrous to nitric acid, and the nitrogen is estimated by the Schultze-Tiemann method. A good gun-cotton in two hours should not give more than 2.5 c.c. of nitric oxide and a collodion cotton not more than 2.0 c.c.

A. Dupré came to the following conclusion concerning the test (*Annual Report of H. M. Inspectors of Explosives*, 1904, **29**, 28; also 1905, **30**, 28): "It was found, in the first place, that duplicate experiments with the same sample of gun-cotton gave as a rule very concordant results, but that, in the second place, the test was influenced to a considerable degree by variation in the percentage of moisture in the samples tested. This was more especially found to be the case when the sample was not perfectly purified, and might thus easily lead to mistaken decisions with regard to the rejection or approval of samples near the limit of purity, unless certain limits of moisture are very rigidly observed.

"The test is scarcely influenced at all by the presence of perchloride of mercury, which, as is well known, renders our heat test inapplicable, but like this latter test it is greatly influenced by the presence of urea. The test is also greatly affected by the condition of the gun-cotton tested, *i. e.*, whether gelatinised or simply pulped, the former giving far lower results than the latter. The test in its present form is not applicable to nitroglycerin preparations or to such as contain nitrates, and does not distinguish so sharply as the heat test between the various stages of washing of gun-cotton. Lastly, in spite of all care taken, tests made on the same sample gave occasionally widely different results, due perhaps to the fact that the products of decomposition are left in contact with the sample throughout the test, whereby very small difference in the rate of decomposition at the beginning of the experiment would be greatly aggravated at the end."

Instead of determining the nitrogen acids collected in the cup gasometrically it is simpler to estimate them by titration with standard alkali.

The test has not proved equally successful for the examination of gelatinised powders, and this may be due to the impossibility of removing the moisture without at the same time eliminating the volatile products of decomposition.

F. M. Mayrhofer has proposed (*Z. ges. Schiess u. Sprengstoffw.*, 1918, **13**, 425 and 448), a modification in which he takes the powder in the air-dry state and weighs out 2 grm., if possible in one piece, and heats at 132° as in the ordinary B. and J. test, but in the cup he places potassium iodide solution which he afterwards titrates with thiosulphate. In the case of nitroglycerin powders the test is carried out in duplicate, one tube being prepared as just stated but the other differs in that 0.5 to 1 5 c.c. of water is added to the explosive. It is stated that if the powder be stable there is no great difference in the results yielded by the two tubes but if it be unstable the tube to which the water has been added shows a great increase in the evolution of nitrogen in not less than 5 hours' heating. W. Will corroborates this (*Z. ges. Schiess u. Sprengstoffw.*, 1919, **14**, 61), but tests carried out in my own laboratory have given very irregular results.

Sy's Test.—In this test, which is known also as the "U. S. Army Ordnance 115° test," whole pieces of nitro-cellulose powder are weighed out on watch glasses and then placed in a bath at 115° for eight hours. The sample is reweighed and the heating is repeated for a further eight hours next day, and so on for six days (See A. P. Sy, *J. Amer. Chem. Soc.*, 1903, 549; *J. Frank. Inst.*, 1903, p. 161; E. M. Weaver, *Military Explosives*, 4th Ed., 1917, 188). The loss of weight must not exceed that permitted for powder of that particular web thickness:

Web Thickness	Loss, Per Cent.
.020 inch	6.8
.060	7.45
.100	8 1
.140	8.5

The temperature of the bath should not vary more than ½° from 115°; it may be maintained by filling the space between the walls of the oven with a mixture of toluene and xylene and boiling it under an inverted condenser.

Vacuum Tests.—A number of workers have determined the rate of evolution of gas by explosives in vacuo, but the best of such methods appears to be that worked out in the Research Department, Woolwich, and described by R. C. Farmer (*Trans. Chem. Soc.*, 1920, **117**, 1432. See also his later papers ibid., 1920, **117**, 1603; 1922, **121**, 174 and C. N. Hinshelwood, 1921, **119**, 721), who gives references to the earlier literature. Such methods are, however, used more for special investigations than for routine determinations of stability. The figures given at the commencement of this section on stability were obtained in the apparatus described by Farmer.

CHEMICAL METHODS

The above methods all depend on measuring the rate of decomposition of the explosive on heating. There is perhaps more hope in methods based on ascertaining the changes in composition that have been produced by its deterioration during the storage that has already taken place. Methods for the examination of diphenylamine and the products into which it is converted have already been described. Similar tests could be worked out for other stabilisers. A. Angeli and F. G. Erani test ballistite and other smokeless powders for acidity by immersing thin shavings in a dilute solution of dimethylaminoazobenzene (*Gazz. Chim. Ital.*, 1920, **50**, 139; *Atti R. Acad. Lincei*, 1918, **27**, 164). If acid the cut surfaces are coloured red. This appears promising but experience is lacking to show whether it is reliable.

Estimations of nitrogen and of calorific power have been made with old samples of poudre B to show the progress of decomposition, but with cordite the differences are too small to be of use.

Physical and Mechanical Tests.—So many of these are in use that it is impossible to deal with most of them even briefly in this work, and the special books on explosives must be consulted (See Marshall's Explosives, 2nd Ed., 1917; also *U. S. Bureau of Mines Technical paper* 186, 1918, Methods for the Routine Work in the Explosives Physical Laboratory of the Bureau of Mines). The sensitiveness to impact, friction, detonation and to heat in various forms are all of importance, as also is the liability to absorb moisture or to separate one or more of the ingredients. The heat of explosion and the volume of gas given off should be known in order to characterise an explosive, as also the power, which can be calculated from these data or determined directly by the Trauzl test, ballistic pendulum and by other methods. The velocity of detonation also is of fundamental importance, as it affects the violence or "brisance," which, however, can also be tested for directly. There are various special methods for testing different varieties of ammunition.

Apparent Density.—This is a property of fundamental importance, for in the case of a propellant it affects the rate of burning and therefore the ballistics, and in the case of a high explosive it has a great influence on the velocity of detonation and still more on the brisance. It is not recorded as often as it should be, in spite of the fact that usually it is not difficult to determine.

In the case of black powder the density is usually determined in Bianchi's densimeter, in which the volume is ascertained by the weight of mercury displaced when the powder is under a pressure of nearly one atmosphere after evacuating. This, however, is not suitable for high explosives as one does not want either to remove the air from the pores or to compress it. In the U. S. Bureau of Mines the volume of a blasting cartridge is ascertained by weighing in a small box of sand.

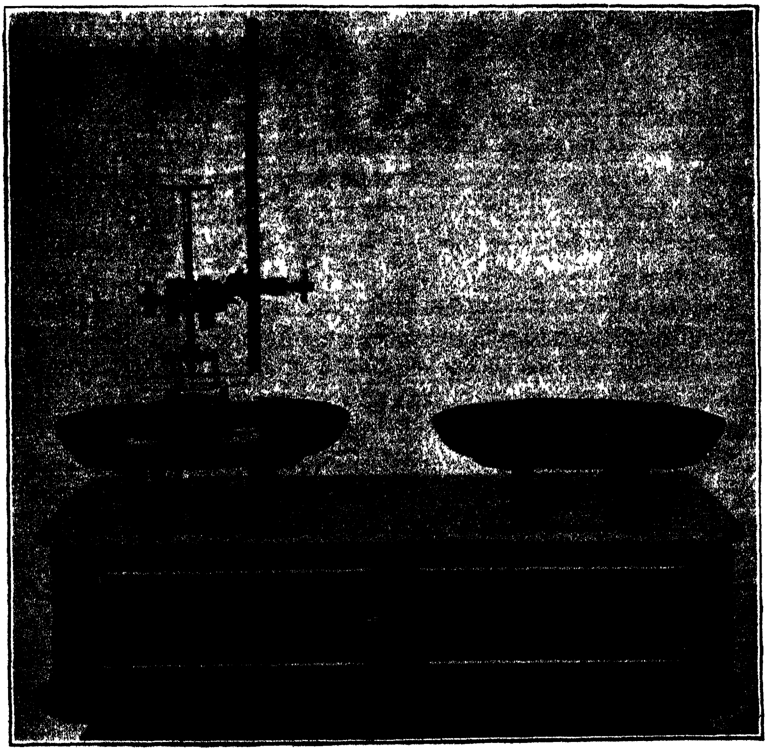

FIG. 36.—Apparatus for determining apparent density.

I have found the instrument shown in Fig. 36 useful for ascertaining the volume of small pieces of blasting explosives or shell fillings. It is made entirely of steel and contains of a shallow inverted cone with a hole in the apex to allow air bubbles to escape. This is supported from a rod having a screw cut on it and working through a large nut which can be held by a clamp. The rod ends below in a point. In the illustration it is shown in use for determining the volume of a cork by immersion in water, but for explosives the liquid generally used is mercury. The basin of mercury is counterpoised on the scales with the instrument screwed down so far that the point just touches its reflection in the liquid. Then a piece of the explosive the weight of which is known to about 0.01 grm. is placed under the inverted cone and the weights and screw are adjusted. The difference of weight of course is the weight of an equal volume of mercury.

EXUDATION

Explosives containing nitroglycerin are liable under certain circumstances to sweat out some of this substance, and this is a source of serious danger. Kieselguhr dynamite, for instance, gives up practically the whole of its nitroglycerin if it becomes wet. If the guhr be over or under calcined, or if it be insufficiently absorbent, this tendency is much increased.

Gelatinised explosives are liable to become too liquid at a moderately high temperature if the collodion cotton be of an unsuitable character, or if there be not enough of it. The Home Office prescribes that these explosives shall pass a test which is identical with the American Liquefaction Test described above.

The German Railway Commission specifies down that a complete cartridge shall be kept for five days at 30°. No nitroglycerin must exude, and after cooling the cartridge must be unchanged.

In the case of one particular brand of gelatinised explosives its great tendency to exude was traced by Hake to the use of wrappers of parchment paper made from wood pulp (*J. Soc. Chem. Ind.*, 1905, p. 915). Such paper in the process of parchmentising with sulphuric acid develops pores through which the nitroglycerin is drawn by capillary action and forms beads on the outside of the wrapper. Parchment paper made from cotton rags is free from this defect. In Germany wrappers of paraffined paper are used.

American dynamites, containing as they do ungelatinised nitroglycerin absorbed in a comparatively small quantity of wood-meal together with a deliquescent salt, are particularly liable to exude. The matter was investigated in 1908 by the "Bureau for the safe Transportation of Explosives," and three different tests have been adopted, descriptions of which will be found in U. S. Bureau of Explosives Reports 2 and 4, 1909 and 1911.

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TABLE FOR

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES.

All degrees are + unless otherwise marked.

1° F. = 0.55° C.
1° C. = 1.8° F.

C.	F.	C.	F.	C.	F.
2000.0	3632.0	1371.1	2500.0	800.0	1472.0
1900.0	3452.0	1300.0	2372.0	760.0	1400.0
1800.0	3272.0	1200.0	2192.0	704.4	1300.0
1700.0	3092.0	1100.0	2012.0	700.0	1292.0
1648.7	3000.0	1093.3	2000.0	648.8	1200.0
1600.0	2912.0	1000.0	1832.0	600 0	1112.0
1500.0	2732.0	900.0	1652.0	593.3	1100.0
1400.0	2552.0	815.5	1500.0	537.7	1000.0

C.	F.	C.	F.	C.	F.
537.7	1000 0	421.1	790.0	304.4	580.0
532.1	990.0	420.0	788.0	300.0	572.0
530.0	986.0	415.6	780.0	298.6	570.0
526.6	980.0	410.0	770.0	293.1	560.0
521.1	970.0	404.4	760.0	290.0	554.0
520.0	968.0	400.0	752.0	287.6	550.0
515.6	960.0	398.6	750.0	282.1	540.0
510.0	950.0	393.1	740.0	280.0	536.0
504.4	940.0	390.0	734.0	276.6	530.0
500.0	932.0	387.6	730 0	271.1	520.0
498.0	930.0	382.1	720.0	270.0	518.0
493.2	920.0	380.0	716.0	265.6	510.0
490.0	914.0	376.6	710.0	260.0	500.0
487.7	910.0	371.1	700.0	259 4	499.0
482.1	900.0	370.0	698.0	259.0	498.2
480.0	896.0	365.6	690.0	258.9	498.0
476.6	890.0	360.0	680.0	258.3	497.0
471.1	880.0	354.4	670.0	258.0	496.4
470.0	878.0	350.0	662.0	257.8	496.0
465.6	870.0	348.6	660.0	257.2	495.0
460.0	860.0	343.1	650.0	257.0	494.6
454.4	850 0	340.0	644.0	256.6	494.0
450.0	842.0	337.6	640.0	256.1	493.0
448.6	840.0	332.1	630.0	256.0	492.8
443.1	830.0	330.0	626.0	255.5	492.0
440.0	824.0	326.6	620.0	255.0	491.0
437.6	820.0	321.1	610.0	254.4	490.0
432.1	810.0	320.0	609.0	254.0	489.2
430.0	806.0	315.6	600.0	253.9	489.0
426.6	800.0	310.0	590.0	253.3	488.0

C.	F.	C.	F.	C.	F.
253.0	487.4	236.6	458.0	220.0	428.0
252.8	487.0	236.1	457.0	219.4	427.0
252.2	486.0	236.0	456.8	219.0	426.2
252.0	485.6	235.5	456.0	218.9	426.0
251.6	485.0	235.0	455.0	218.3	425.0
251.1	484.0	234.4	454.0	218.0	424.4
251.0	483.8	234.0	453.2	217.8	424.0
250.5	483.0	233.9	453.0	217.2	423.0
250.0	482.0	233.3	452.0	217.0	422.6
249.4	481.0	233.0	451.4	216.6	422.0
249.0	480.2	232.8	451.0	216.1	421.0
248.9	480.0	232.2	450.0	216.0	420.8
248.3	479.0	232.0	449.6	215.5	420.0
248.0	478.4	231.6	449.0	215.0	419.0
247.8	478.0	231.1	448.0	214.4	418.0
247.2	477.0	231.0	447.8	214.0	417.2
247.0	476.6	230.5	447.0	213.9	417.0
246.6	476.0	230.0	446.0	213.3	416.0
246.1	475.0	229.4	445.0	213.0	415.4
246.0	474.8	229.0	444.2	212.8	415.0
245.5	474.0	228.9	444.0	212.2	414.0
245.0	473.0	228.3	443.0	212.0	413.6
244.4	472.0	228.0	442.4	211.6	413.0
244.0	471.2	227.8	442.0	211.1	412.0
243.9	471.0	227.2	441.0	211.0	411.8
243.3	470.0	227.0	440.6	210.5	411.0
243.0	469.4	226.6	440.0	210.0	410.0
242.8	469.0	226.1	439.0	209.4	409.0
242.2	468.0	226.0	438.8	209.0	408.2
242.0	467.6	225.5	438.0	208.9	408.0
241.6	467.0	225.0	437.0	208.3	407.0
241.1	466.0	224.4	436.0	208.0	406.4
241.0	465.8	224.0	435.2	207.8	406.0
240.5	465.0	223.9	435.0	207.2	405.0
240.0	464.0	223.3	434.0	207.0	404.6
239.4	463.0	223.0	433.4	206.6	404.0
239.0	462.2	222.8	433.0	206.1	403.0
238.9	462.0	222.2	432.0	206.0	402.8
238.3	461.0	222.0	431.6	205.5	402.0
238.0	460.4	221.6	431.0	205.0	401.0
237.8	460.0	221.1	430.0	204.4	400.0
237.2	459.0	221.0	429.8	204.0	399.2
237.0	458.6	220.5	429.0	203.9	399.0

C.	F.	C.	F.	C.	F.
203.3	398.0	187.0	368.6	170.5	339.0
203.0	397.4	186.6	368.0	170.0	338.0
202.8	397.0	186.1	367.0	169.4	337.0
202.2	396.0	186.0	366.8	169.0	336.2
202.0	395.6	185.5	366.0	168.9	336.0
201.6	395.0	185.0	365.0	168.3	335.0
201.1	394.0	184.4	364.0	168.0	334.4
201.0	393.8	184.0	363.2	167.8	334.0
200.5	393.0	183.9	363.0	167.2	333.0
200.0	392.0	183.3	362.0	167.0	332.6
199.4	391.0	183.0	361.4	166.6	332.0
199.0	390.2	182.8	361.0	166.1	331.0
198.9	390.0	182.2	360.0	166.0	330.8
198.3	389.0	182.0	359.6	165.5	330.0
198.0	388.4	181.6	359.0	165.0	329.0
197.8	388.0	181.1	358.0	164.4	328.0
197.2	387.0	181.0	357.8	164.0	327.2
197.0	386.6	180.5	357.0	163.9	327.0
196.6	386.0	180.0	356.0	163.3	326.0
196.1	385.0	179.4	355.0	163.0	325.4
196.0	384.8	179.0	354.2	162.8	325.0
195.5	384.0	178.9	354.0	162.2	324.0
195.0	383.0	178.3	353.0	162.0	323.6
194.4	382.0	178.0	352.4	161.6	323.0
194.0	381.2	177.8	352.0	161.1	322.0
193.9	381.0	177.2	351.0	161.0	321.8
193.3	380.0	177.0	350.6	160.5	321.0
193.0	379.4	176.6	350.0	160.0	320.0
192.8	379.0	176.1	349.0	159.4	319.0
192.2	378.0	176.0	348.8	159.0	318.2
192.0	377.6	175.5	348.0	158.9	318.0
191.6	377.0	175.0	347.0	158.3	317.0
191.1	376.0	174.4	346.0	158.0	316.4
191.0	375.8	174.0	345.2	157.8	316.0
190.5	375.0	173.9	345.0	157.2	315.0
190.0	374.0	173.3	344.0	157.0	314.6
189.4	373.0	173.0	343.4	156.6	314.0
189.0	372.2	172.8	343.0	156.1	313.0
188.9	372.0	172.2	342.0	156.0	312.8
188.3	371.0	172.0	341.6	155.5	312.0
188.0	370.4	171.6	341.0	155.0	311.0
187.8	370.0	171.1	340.0	154.4	310.0
187.2	369.0	171.0	339.8	154.0	309.2

C.	F.	C.	F.	C.	F.
153.9	309.0	137.2	279.0	121.0	249.8
153.3	308.0	137.0	278.6	120.5	249.0
153.0	307.4	136.6	278.0	120.0	248.0
152.8	307.0	136.1	277.0	119.4	247.0
152.2	306.0	136.0	276.8	119.0	246.2
152.0	305.6	135.5	276.0	118.9	246.0
151.6	305.0	135.0	275.0	118.3	245.0
151.1	304.0	134.4	274.0	118.0	244.4
151.0	303.8	134.0	273.2	117.8	244.0
150.5	303.0	133.9	273.0	117.2	243.0
150.0	302.0	133.3	272.0	117.0	242.6
149.4	301.0	133.0	271.4	116.6	242.0
149.0	300.2	132.8	271.0	116.1	241.0
148.9	300.0	132.2	270.0	116.0	240.8
148.3	299.0	132.0	269.6	115.5	240.0
148.0	298.4	131.6	269.0	115.0	239.0
147.8	298.0	131.1	268.0	114.4	238.0
147.2	297.0	131.0	267.8	114.0	237.2
147.0	296.6	130.5	267.0	113.9	237.0
146.6	296.0	130.0	266.0	113.3	236.0
146.1	295.0	129.4	265.0	113.0	235.4
146.0	294.8	129.0	264.2	112.8	235.0
145.5	294.0	128.9	264.0	112.2	234.0
145.0	293.0	128.3	263.0	112.0	233.6
144.4	292.0	128.0	262.4	111.6	233.0
144.0	291.2	127.8	262.0	111.1	232.0
143.9	291.0	127.2	261.0	111.0	231.8
143.3	290.0	127.0	260.6	110.5	231.0
143.0	289.4	126.6	260.0	110.0	230.0
142.8	289.0	126.1	259.0	109.4	229.0
142.2	288.0	126.0	258.8	109.0	228.2
142.0	287.6	125.5	258.0	108.9	228.0
141.6	287.0	125.0	257.0	108.3	227.0
141.1	286.0	124.4	256.0	108.0	226.4
141.0	285.8	124.0	255.2	107.8	226.0
140.5	285.0	123.9	255.0	107.2	225.0
140.0	284.0	123.3	254.0	107.0	224.6
139.4	283.0	123.0	253.4	106.6	224.0
139.0	282.2	122.8	253.0	106.1	223.0
138.9	282.0	122.2	252.0	106.0	222.8
138.3	281.0	122.0	251.6	105.5	222.0
138.0	280.4	121.6	251.0	105.0	221.0
137.8	280.0	121.1	250.0	104.4	220.0

C.	F.	C.	F.	C.	F.
104.0	219.2	87.8	190.0	71.1	160.0
103.9	219.0	87.2	189.0	71.0	159.8
103.3	218.0	87.0	188.6	70.5	159.0
103.0	217.4	86.6	188.0	70.0	158.0
102.8	217.0	86.1	187.0	69.4	157.0
102.2	216.0	86.0	186.8	69.0	156.2
102.0	215.6	85.5	186.0	68.9	156.0
101.6	215.0	85.0	185.0	68.3	155.0
101.1	214.0	84.4	184.0	68.0	154.4
101.0	213.8	84.0	183.2	67.8	154.0
100.5	213.0	83.9	183.0	67.2	153.0
100.0	**212.0**	83.3	182.0	67.0	152.6
99.4	211.0	83.0	181.4	66.6	152.0
99.0	210.2	82.8	181.0	66.1	151.0
98.9	210.0	82.2	180.0	66.0	150.8
98.3	209.0	82.0	179.6	65.5	150.0
98.0	208.4	81.6	179.0	65.0	149.0
97.8	208.0	81.1	178.0	64.4	148.0
97.2	207.0	81.0	177.8	64.0	147.2
97.0	206.6	80.5	177.0	63.9	147.0
96.6	206.0	80.0	176.0	63.3	146.0
96.1	205.0	79.4	175.0	63.0	145.4
96.0	204.8	79.0	174.2	62.8	145.0
95.5	204.0	78.9	174.0	62.2	144.0
95.0	203.0	78.3	173.0	62.0	143.6
94.4	202.0	78.0	172.4	61.6	143.0
94.0	201.2	77.8	172.0	61.1	142.0
93.9	201.0	77.2	171.0	61.0	141.8
93.3	200.0	77.0	170.6	60.5	141.0
93.0	199.4	76.6	170.0	60.0	140.0
92.8	199.0	76.1	169.0	59.4	139.0
92.2	198.0	76.0	168.8	59.0	138.2
92.0	197.6	75.5	168.0	58.9	138.0
91.6	197.0	75.0	167.0	58.3	137.0
91.1	196.0	74.4	166.0	58.0	136.4
91.0	195.8	74.0	165.2	57.8	136.0
90.5	195.0	73.9	165.0	57.2	135.0
90.0	194.0	73.3	164.0	57.0	134.6
89.4	193.0	73.0	163.4	56.6	134.0
89.0	192.2	72.8	163.0	56.1	133.0
88.9	192.0	72.2	162.0	56.0	132.8
88.3	191.0	72.0	161.6	55.5	132.0
88.0	190.4	71.6	161.0	55.0	131.0

C.	F.	C.	F.	C.	F.
−44.4	−48.0	−61.1	−78.0	−77.7	−108.0
−45.0	−49.0	−61.6	−79.0	−78.0	−108.4
−45.5	−50.0	−62.0	−79.6	−78.3	−109.0
−46.0	−50.8	−62.2	−80.0	−78.8	−110.0
−46.1	−51.0	−62.7	−81.0	−79.0	−110.2
−46.6	−52.0	−63.0	−81.4	−79.4	−111.0
−47.0	−52.6	−63.3	−82.0	−80.0	−112.0
−47.2	−53.0	−63.8	−83.0	−80.5	−113.0
−47.7	−54.0	−64.0	−83.2	−81.0	−113.8
−48.0	−54.4	−64.4	−84.0	−81.1	−114.0
−48.3	−55.0	−65.0	−85.0	−81.6	−115.0
−48.8	−56.0	−65.5	−86.0	−82.0	−115.6
−49.0	−56.2	−66.0	−86.8	−82.2	−116.0
−49.4	−57.0	−66.1	−87.0	−82.7	−117.0
−50.0	−58.0	−66.6	−88.0	−83.0	−117.4
−50.5	−59.0	−67.0	−88.6	−83.3	−118.0
−51.0	−59.8	−67.2	−89.0	−83.8	−119.0
−51.1	−60.0	−67.7	−90.0	−84.0	−119.2
−51.6	−61.0	−68.0	−90.4	−84.4	−120.0
−52.0	−61.6	−68.3	−91.0	−85.0	−121.0
−52.2	−62.0	−68.8	−92.0	−85.5	−122.0
−52.7	−63.0	−69.0	−92.2	−86.0	−122.8
−53.0	−63.4	−69.4	−93.0	−86.1	−123.0
−53.3	−64.0	−70.0	−94.0	−86.6	−124.0
−53.8	−65.0	−70.5	−95.0	−87.0	−124.6
−54.0	−65.2	−71.0	−95.8	−87.2	−125.0
−54.4	−66.0	−71.1	−96.0	−87.7	−126.0
−55.0	−67.0	−71.6	−97.0	−88.0	−126.4
−55.5	−68.0	−72.0	−97.6	−88.3	−127.0
−56.0	−68.8	−72.2	−98.0	−88.8	−128.0
−56.1	−69.0	−72.7	−99.0	−89.0	−128.2
−56.6	−70.0	−73.0	−99.4	−89.4	−129.0
−57.0	−70.6	−73.3	−100.0	−90.0	−130.0
−57.2	−71.0	−73.8	−101.0	−90.5	−131.0
−57.7	−72.0	−74.0	−101.2	−91.0	−131.8
−58.0	−72.4	−74.4	−102.0	−91.1	−132.0
−58.3	−73.0	−75.0	−103.0	−91.6	−133.0
−58.8	−74.0	−75.5	−104.0	−92.0	−133.6
−59.0	−74.2	−76.0	−104.8	−92.2	−134.0
−59.4	−75.0	−76.1	−105.0	−92.7	−135.0
−60.0	−76.0	−76.6	−106.0	−93.0	−135.4
−60.5	−77.0	−77.0	−106.6	−93.3	−136.0
−61.0	−77.8	−77.2	−107.0	−93.8	−137.0

C.	F.	C.	F.	C.	F.
5.0	41.0	−11.6	11.0	−28.0	−18.4
4.4	40.0	−12.0	10.4	−28.3	−19.0
4.0	**39.2**	−12.2	10.0	−28.9	−20.0
3.9	39.0	−12.7	9.0	−29.0	−20.2
3.3	38.0	−13.0	8.6	−29.4	−21.0
3.0	37.4	−13.3	8.0	−30.0	−22.0
2.7	37.0	−13.9	7.0	−30.5	−23.0
2.2	36.0	−14.0	6.8	−31.0	−23.8
2.0	35.6	−14.4	6.0	−31.1	−24.0
1.6	35.0	−15.0	5.0	−31.6	−25.0
1.1	34.0	−15.5	4.0	−32.0	−25.6
1.0	33.8	−16.0	3.2	−32.2	−26.0
0.6	33.0	−16.1	3.0	−32.7	−27.0
0.0	**32.0**	−16.6	2.0	−33.0	−27.4
−0.5	31.0	−17.0	1.4	−33.3	−28.0
−1.0	30.2	−17.2	1.0	−33.9	−29.0
−1.1	30.0	**−17.7**	**0.0**	−34.0	−29.2
−1.6	29.0	−18.0	−0.4	−34.4	−30.0
−2.0	28.4	−18.3	−1.0	−35.0	−31.0
−2.2	28.0	−18.8	−2.0	−35.5	−32.0
−2.7	27.0	−19.0	−2.2	−36.0	−32.8
−3.0	26.6	−19.4	−3.0	−36.1	−33.0
−3.3	26.0	−20.0	−4.0	−36.6	−34.0
−3.9	25.0	−20.5	−5.0	−37.0	−34.6
−4.0	24.8	−21.0	−5.8	−37.2	−35.0
−4.4	24.0	−21.1	−6.0	−37.7	−36.0
−5.0	23.0	−21.6	−7.0	−38.0	−36.4
−5.5	22.0	−22.0	−7.6	−38.3	−37.0
−6.0	21.2	−22.2	−8.0	−38.9	−38.0
−6.1	21.0	−22.7	−9.0	−39.0	−38.2
−6.6	20.0	−23.0	−9.4	−39.4	−39.0
−7.0	19.4	−23.3	−10.0	**−40.0**	**−40.0**
−7.2	19.0	−23.9	−11.0	−40.5	−41.0
−7.7	18.0	−24.0	−11.2	−41.0	−41.8
−8.0	17.6	−24.4	−12.0	−41.1	−42.0
−8.3	17.0	−25.0	−13.0	−41.6	−43.0
−8.9	16.0	−25.5	−14.0	−42.0	−43.6
−9.0	15.8	−26.0	−14.8	−42.2	−44.0
−9.4	15.0	−26.1	−15.0	−42.7	−45.0
−10.0	14.0	−26.6	−16.0	−43.0	−45.4
−10.5	13.0	−27.0	−16.6	−43.3	−46.0
−11.0	12.2	−27.2	−17.0	−43.8	−47.0
−11.1	12.0	−27.7	−18.0	−44.0	−47.2

C.	F.	C.	F.	C.	F.
54.4	130.0	38.0	100.4	21.6	71.0
54.0	129.2	37.8	100.0	21.1	70.0
53.9	129.0	37.2	99.0	21.0	69.8
53.3	128.0	**37.0**	**98.6**	20.6	69.0
53.0	127.4	36.6	98.0	20.0	68.0
52.8	127.0	36.1	97.0	19.4	67.0
52.2	126.0	36.0	96.8	19.0	66.2
52.0	125.6	35.5	96.0	18.9	66.0
51.6	125.0	35.0	95.0	18.4	65.0
51.1	124.0	34.4	94.0	18.0	64.4
51.0	123.8	34.0	93.2	17.7	64.0
50.5	123.0	33.9	93.0	17.2	63.0
50.0	122.0	33.3	92.0	17.0	62.6
49.4	121.0	33.0	91.4	16.6	62.0
49.0	120.2	32.8	91.0	16.1	61.0
48.9	120.0	32.2	90.0	16.0	60.8
48.3	119.0	32.0	89.6	**15.55**	**60.0**
48.0	118.4	31.6	89.0	15.0	59.0
47.8	118.0	31.1	88.0	14.4	58.0
47.2	117.0	31.0	87.8	14.0	57.2
47.0	116.6	30.5	87.0	13.9	57.0
46.6	116.0	30.0	86.0	13.3	56.0
46.1	115.0	29.6	85.0	13.0	55.4
46.0	114.8	29.0	84.2	12.7	55.0
45.5	114.0	28.9	84.0	12.2	54.0
45.0	113.0	28.3	83.0	12.0	53.6
44.4	112.0	28.0	82.4	11.6	53.0
44.0	111.2	27.9	82.0	11.1	52.0
43.9	111.0	27.3	81.0	11.0	51.8
43.3	110.0	27.0	80.6	10.6	51.0
43.0	109.4	26.7	80.0	10.0	50.0
42.8	109.0	26.2	79.0	9.4	49.0
42.2	108.0	26.0	78.8	9.0	48.2
42.0	107.6	25.6	78.0	8.9	48.0
41.6	107.0	25.0	77.0	8.3	47.0
41.1	106.0	24.4	76.0	8.0	46.4
41.0	105.8	24.0	75.2	7.7	46.0
40.5	105.0	23.9	75.0	7.2	45.0
40.0	104.0	23.3	74.0	7.0	44.6
39.4	103.0	23.0	73.4	6.6	44.0
39.0	102.2	22.7	73.0	6.1	43.0
38.9	102.0	22.2	72.0	6.0	42.8
38.3	101.0	22.0	71.6	5.6	42.0

C.	F.	C.	F.	C.	F.
-94.0	-137.2	-111.0	-167.8	-127.2	-197.0
-94.4	-138.0	-111.1	-168.0	-127.7	-198.0
-95.0	-139.0	-111 6	-169.0	-128.0	-198.4
-95.5	-140.0	-112.0	-169.6	-128.3	-199.0
-96.0	-140 8	-112.2	-170.0	-128.8	-200.0
-96.1	-141.0	-112.7	-171 0	-129 0	-200.2
-96.6	-142.0	-113.0	-171.4	-129 4	-201.0
-97.0	-142.6	-113.3	-172.0	-130.0	-202.0
-97.2	-143.0	-113.8	-173.0	-130.5	-203.0
-97.7	-144.0	-114.0	-173.2	-131.0	-203.8
-98.0	-144.4	-114.4	-174.0	-131.1	-204.0
-98.3	-145.0	-115.0	-175.0	-131.6	-205.0
-98.8	-146.0	-115.5	-176.0	-132.0	-205.6
-99.0	-146.2	-116.0	-176.8	-132.2	-206.0
-99 4	-147.0	-116.1	-177.0	-132.7	-207.0
-100.0	-148.0	-116.6	-178.0	-133.0	-207.4
-100.5	-149.0	-117.0	-178.6	-133.3	-208.0
-101.0	-149.8	-117.2	-179.0	-133.8	-209.0
-101.1	-150.0	-117.7	-180.0	-134.0	-209.2
-101.6	-151.0	-118.0	-180.4	-134.4	-210.0
-102.0	-151.6	-118.3	-181.0	-135.0	-211.0
-102.2	-152.0	-118.8	-182.0	-135.5	-212.0
-102.7	-153.0	-119.0	-182.2	-136.0	-212.8
-103.0	-153.4	-119.4	-183.0	-136.1	-213.0
-103.3	-154.0	-120.0	-184.0	-136.6	-214.0
-103.8	-155.0	-120.5	-185.0	-137.0	-214.6
-104.0	-155.2	-121.0	-185.8	-137.2	-215.0
-104.4	-156.0	-121.1	-186.0	-137.7	-216.0
-105.0	-157.0	-121.6	-187.0	-138.0	-216.4
-105 5	-158.0	-122.0	-187.6	-138.3	-217.0
-106.0	-158.8	-122.2	-188.0	-138.8	-218.0
-106.1	-159.0	-122.7	-189.0	-139.0	-218.2
-106.6	-160.0	-123.0	-189.4	-139.4	-219.0
-107.0	-160.6	-123.3	-190.0	-140.0	-220.0
-107.2	-161.0	-123.8	-191.0	-140.5	-221.0
-107.7	-162.0	-124.0	-191.2	-141.0	-221.8
-108.0	-162.4	-124.4	-192.0	-141.1	-222.0
-108.3	-163.0	-125.0	-193.0	-141.6	-223.0
-108.8	-164.0	-125.5	-194.0	-142.0	-223.6
-109.0	-164.2	-126.0	-194.8	-142.2	-224.0
-109.4	-165.0	-126.1	-195.0	-142.7	-225.0
-110.0	-166.0	-126.6	-196.0	-143.0	-225.4
-110.5	-167.0	-127.0	-196.6	-143.3	-226.0

C.	F.	C.	F.	C.	F.
−143.8	−227.0	−149.0	−236.2	−154.4	−246.0
−144.0	−227.2	−149.4	−237.2	−155.0	−247.0
−144.4	−228.0	−150.0	−238.0	−155.5	−248.0
−145.0	−229.0	−150.5	−239.0	−156.0	−248.8
−145.5	−230.0	−151.0	−239.8	−156.1	−249.0
−146.0	−230.8	−151.1	−240.0	−156.6	−250.0
−146.1	−231.0	−151.6	−241.0	−157.0	−250.6
−146.6	−232.0	−152.0	−241.6	−157.2	−251.0
−147.0	−232.6	−152.2	−242.0	−157.7	−252.0
−147.2	−233.0	−152.7	−243.0	−158.0	−252.4
−147.7	−234.0	−153.0	−243.4	−158.3	−253.0
−148.0	−234.4	−153.3	−244.0	−158.8	−254.0
−148.3	−235.0	−153.8	−245.0	−159.0	−254.2
−148.8	−236.0	−154.0	−245.2	−159.4	−255.0

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